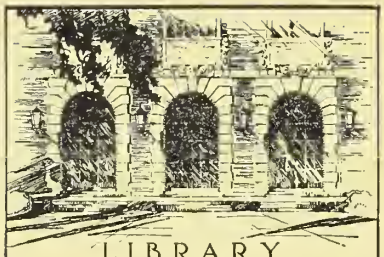

INORGANIC SEMINARS

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THESIS REPORT

I. THE STRUCTURE AND PROPERTIES OF TETRAALKYL-2-TETRAZENES

II. SOME SUBSTITUTION REACTIONS OF TRIMERIC PHOSPHONITRILIC CHLORIDE

William Earnest Bull August, 1957

PART I

Tetramethyl-2-tetrazene was prepared by the oxidation of unsymmetrical dimethylhydrazine with mercuric oxide. Tetramethyl-2-tetrazene is a basic substance and forms salts which are unstable toward hydrolysis and heat. It forms coordination compounds with heavy metal ions; the tetramethyl-2-tetrazene mercuric bromide complex is monomeric in benzene and a nonconductor in ethanol.

Tetramethyl-2-tetrazene has been shown by a spectrophotometric procedure to be produced by the incomplete oxidation of dimethylhydrazine with a variety of oxidizing agents. Autoxidation of dimethylhydrazine has been shown to produce the corresponding 2-tetrazene.

Reduction of tetramethyl-2-tetrazene in liquid ammonia required four moles of sodium, but no product could be isolated from the reduction mixture.

Tetramethyl-2-tetrazene and tetraethyl-2-tetrazene were found to give ultraviolet absorbancy maxima at 277 mμ and 285 mμ in ethanol with molar absorptivities (a_M) of 8.3×10^3 and 5.4×10^3, respectively. The absorbancy maxima of tetraalkyl-2-tetrazenes were found to shift to higher frequencies as more protonic solvents were employed. This property was utilized to determine a value of 5.13 for the pK_b of tetraethyl-2-tetrazene.

The characteristic infrared absorption spectra of several tetraalkyl-2-tetrazenes, their derivatives, and related compounds were obtained and group absorption frequencies were assigned. The absorption bands occurring at 1450 cm^{-1} and 1438 cm^{-1} in the spectrum of tetramethyl-2-tetrazene are assigned to the -N=N- linkage, along with those occurring in the 1400 cm^{-1} region for the cadmium halide complexes and the oxalate salt.

The electric moment of tetramethyl-2-tetrazene was found to have a value of 1.2 ± 0.1 D. by two different methods. This value, however, does not permit the assignment of either a cis- or a trans-structure to the hydronitrogen.

PART II

The chlorine atoms on the trimeric phosphonitrilic ring have been shown to be less reactive than previous workers have indicated. The reactivity of the chlorine atoms decreases progressively as the number of non-halogen substituents on the ring is increased. The

ease and the degree of solvolysis of the halides has been related to the base strength of the solvolytic agent and to its effective concentration.

The preparation of a tri-substituted derivative, tri(phosphonitrile) trichloro-tris-diethylamide, has shown that pairwise replacement of the chlorine atoms is not necessarily always indicated.

The action of sodium in liquid ammonia on trimeric phosphonitrilic chloride results in the cleavage of the phosphonitrilic ring as evidenced by the reaction mole ratio of 8:1 of sodium to triphosphonitrilic chloride and the formation of phosphine as a reduction product.

The characteristic infrared absorption spectra of several N-substituted phosphonitrilic derivatives were obtained and all were found to possess an absorption band in the region of 1200 cm^{-1}. Since this frequency had previously been assigned to the phosphorus-nitrogen ring vibrations, retention of the ring structure in these derivatives is verified.

THESIS REPORT

THE STEREOCHEMISTRY OF SOME COBALT (III) COMPLEXES CONTAINING OPTICALLY ACTIVE LIGANDS

Bennie Anthony Ferrone August, 1957

The initial objective of this work was a study of the cobalt(III) complexes of optically active 1,2-diphenylethylenediamine with a view toward using them in studies on preferential coordination. The most convenient starting material for this study was trans-[Co(d-stien)$_2$ Cl$_2$]Cl (stien → 1,2-diphenylethylenediamine). Resolutions of tartaric acid, propylenediamine, and trans-1,2-diaminocyclohexane were attempted. No resolutions were obtained.

When trans-[Co(d-stien → Cl$_2$]Cl was allowed to react with racemic-1,2-diphenylethylenediamine, resolution of the base seemed to occur; however, on the basis of previous experience, the "wrong" isomer appeared to coordinate preferentially. Investigation of this reaction led to the conclusion that diastereoisomeric species were being produced. A more complete examination required a study of the products of the following reactions:

I. trans-[Co(d-stien)$_2$ Cl$_2$]Cl + 2 d,l-stien →

II. trans-[Co(d-stien)$_2$ Cl$_2$]Cl + l-stien →

III. trans-[Co(d-stien)$_2$ Cl$_2$]Cl + 2 l-stien →

IV. trans-[Co(d-stien)$_2$ Cl$_2$]Cl + 2 meso-stien →

Fractionation of the products of these reactions gave two distinctly different fractions in each case. With the exception of reaction III, Fraction I, or the easily crystallizable fraction, had a positive rotation at the D line of sodium, whereas Fraction II had a negative rotation. In the case of reaction III all products were inactive.

Optical rotatory dispersion curves of all the fractions gave indications that a number of isomers had been isolated. Therefore, each fraction was decomposed, the 1,2-diphenylethylenediamine was recovered, and its optical rotation was determined. This gave evidence for the existence of the isomers D-[Co(d-stien)$_2$(l-stien)]Cl$_3$, L-[Co(d-stien)$_2$(l-stien)]Cl$_3$, D-[Co(d-stien)$_2$(meso-stien)]Cl$_3$, and L-[Co(d-stien)$_2$(meso-stien)]Cl$_3$. In addition, the isomers D-[Co(d-stien)$_2$]Cl$_3$ and L-[Co(d-stien)$_3$]Cl$_3$ were isolated from the reaction

trans-[Co(d-stien)$_2$ Cl$_2$]Cl + d-stien →

It was found that heating an alcoholic solution of D-[Co(d-stien)$_3$]Cl$_3$ under reflux for several hours caused a change in rotation from a high positive value to a negative value. This is

indicative of the fact that although a number of isomers are isolable from this system, they are not of equal stability.

Altogether, evidence was found for twelve of the eighteen isomers possible in the cobalt (III)-1,2-diphenylethylenediamine system.

A study was also undertaken on the cobalt (III) complex of trans-1,2-diaminocyclohexanetetraacetic acid (H_4DCTA). It was hoped that this ligand could be resolved and its active cobalt (III) complex used in the manner of Kirschner's work with the cobalt (III)-ethylenediaminetetraacetate complex (1).

Some difficulty was encountered in preparing the $[Co\ DCTA]^-$ ion, but a convenient synthesis was eventually found. Resolution of this ion was attempted with a number of reagents, but with no success. Resolution of the base was then attempted, but to no avail. A synthesis of the active base from optically active trans-1,2-diaminocyclohexane also failed. Finally, an attempt was made to resolve the $[Co\ DCTA]^-$ ion by the reaction

$$2\ \underline{D},\underline{L}\text{-}[Co\ DCTA]^- + 3\ \underline{l}\text{-pn} \rightarrow \underline{D}\text{-}[Co(\underline{d}\text{-DCTA}]^- + [Co(\underline{l}\text{-pn})_3]^{3+} + \underline{l}\text{-DCTA}'$$

However, this method failed also because of the reduction of the $[Co\ DCTA]^-$ species.

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THESIS REPORT

OBSERVATIONS ON THE RARE EARTHS: CHELATES DERIVED FROM DIAMINE TETRA- AND TRI-ACETIC ACIDS

Earl Philip Horwitz August, 1957

The objects of this present work were to characterize more completely the complexes that can be formed between ethylenediaminetetraacetic acid, abbreviated H_4(EDTA), N-hydroxyethylethylenediaminetriacetic acid, abbreviated H_2(HEDTA), and 1,2-diaminocyclohexanetetraacetic acid, abbreviated H_4(DCTA), and the rare earth metal ions, and to study the nature of the bonding and structures of the complexes thus formed.

Neutralization curves were determined for H_2(HEDTA) and H_4(DCTA) in and without the presence of rare earth metal ions. These curves have shown that stable complexes with a 1:1 ratio of rare earth metal ion to HEDTA or DCTA were formed. Approximate values for the formation constants of these complexes were calculated from data obtained from the titration curves. The formation constants of the rare earth-HEDTA, -EDTA, and -DCTA complexes were correlated with the charge squared divided by the radius of the rare earth metal ions. It was shown that the size and charge of the rare earth metal ion are not the only factors influencing the stability of these rare earth chelates.

Complexes of the type Ln(HEDTA) have been prepared for neodymium, samarium, europium, gadolinium, and yttrium by treating rare earth carbonate with H_3(HEDTA) in a 1:1 rare earth metal ion/HEDTA ratio and precipitating the complex from aqueous solution with isopropyl alcohol. X-ray diffraction studies have shown that the chelate compounds are isomorphous.

Complexes of the type $Ba[Ln(DCTA)]_2$ have been prepared for neodymium, samarium, europium, gadolinium, and yttrium by treating rare earth carbonate first with H_4(DCTA) and then with barium carbonate. The chelate compounds were precipitated from aqueous solution with 95% ethanol. X-ray diffraction studies have shown that the chelate compounds are isomorphous.

Magnetic susceptibilities of a number of rare earth-HEDTA, -EDTA, and -DCTA chelates were measured at room temperature. The generally fair agreement between the magnetic moments of the chelate compounds and the hydrated sulfates indicates that the 4f electrons are not of great significance in the bonding in rare earth chelates of the type studied.

The absorption spectra of aqueous solutions of the chlorides of praseodymium, neodymium, samarium, and europium were measured in the presence of HEDTA and DCTA. It was noted that there is no

correlation between alteration in the absorption spectra of the tripositive rare earth metal ions when complexed with HEDTA, EDTA, and DCTA and the stability of the chelates formed.

Differential thermal analysis has indicated the thermal stabilities of the rare earth-HEDTA and -DCTA chelates with respect to dehydration and decomposition. Dehydration studies of $NH_4[S_m(EDTA)]\cdot 8H_2O$ and $S_m(HEDTA)\cdot 5H_2O$ have shown that one water molecule per chelate molecule is more tenaciously held by the chelate than the rest of the water molecules. This suggests that the water molecule is occupying the sixth coordination position in the coordination sphere.

Infrared absorption spectra of Ln(HEDTA) and $Ba[(DCTA)]_2$ type chelates were obtained. The spectra indicate that all three carboxyl groups in L_n(HEDTA) chelates are complexed. The spectra also indicate the high degree of ionic character in the rare earth-carboxyl linkage.

The lengths of the edges of the unit cell and the number of molecules per unit cell were measured for the orthohombic-hemimorphic crystals of $N_a[Nd(EDTA)]\cdot 8H_2O$. The lengths of the edges of the unit cell were found to be the following: a = 9.87 Å., b = 17.7 Å., and c = 6.22 Å. The crystal was found to contain two molecules per unit cell.

THESIS REPORT

PHYSICAL CHEMICAL STUDIES ON SOME COMPLEX INORGANIC COMPOUNDS

I. The Kinetics Of Aquation Of cis-Dichloro-bis-(Ethylene-Diamine)-Chromium(III) Ion.

II. The Stereochemistry Of Some Triethylenetetramine Complexes.

III. The Reduction Of A Nitro Group Coordinated To Platinum.

Joel Selbin August, 1957

Part I reports a study of the kinetics of acid hydrolysis of cis-$[Cren_2Cl_2]^+$ at pH = 1.0, under various conditions of added electrolytes and at three temperatures. A chloride concentration cell was employed to measure chloride release. The pseudo first order rate constant for the loss of one chloride is given by $k_1 = 9.65 \times 10^{11} \exp. (-21,100/ET)$ sec.$^{-1}$, and $\Delta S^{\neq} = -5.7$ e.u. A value for the specific rate constant for the loss of a second chloride has been estimated. The effects of certain salt additions have been interpreted as support for an S_N1 mechanism. A change in the specific rate constant with initial concentration of complex has been observed and the overall rate found to be proportional to the initial concentration. A possible explanation for this behavior is presented. Results of studies on the change in optical rotation of l-cis-$[Cren_2Cl_2]^+$ are interpreted in terms of an initial aquation without loss of optical activity followed by racemization of the chloroaquo product. The chloroaquo product racemizes at a greater rate than it aquates, indicating that different mechanisms must be operative for the two processes. Analogies with the corresponding cobalt(III) complexes suggest that complexes of the two metals follow similar mechanisms during acid hydrolysis. A suggestion is made as to why chromium(III) complexes resemble cobalt(III) complexes so closely.

Part II presents the results of a study of some triethylenetetramine (trien) complexes of cobalt(III), in which a search was made for a complex having the four amine nitrogens disposed equatorially about the metal ion. Visible and ultraviolet spectra indicated that only one of the three possible stereochemical modifications of the ion $[Co\ trien(NO_2)_2]^+$ was formed, although six different methods were used for its preparation. The data are interpreted as support for a cis structure. However, nine resolving agents were employed in unsuccessful attempts to resolve the ion and thus unequivocal evidence for the cis arrangement was not obtained. Two methods of preparation of the ion $[Co\ trien\ Br_2]^+$ yielded a green product and one method produced a deep gray violet product, both giving the same analysis. By analogy to numerous cis-trans pairs of diacidotetrammine type complexes of cobalt(III) and chromium(III) the green compound is assigned a trans configuration. The planar disposition of the four trien nitrogens is thus

established in the dibromo complex. In the course of this study the first well-established example of a crystalline complex of cobalt(III) containing the quinquidentate coordinating agent, tetraethylenepentamine (tetren) was prepared.

Part III concerns a semi-quantitative polarographic investigation of some cobalt(III) and platinum(II) complexes, each containing a coordinated nitro group. The supporting electrolyte was either tenth molar perchloric acid or tenth molar sodium perchlorate. The purpose of the study was to find evidence for the possibility of reducing a nitro group coordinated to a metal ion, without reducing the metal itself. No success was obtained with a series of cobalt(III) complexes, the reduction of cobalt(III) to cobalt(II) always occurring with subsequent decomposition of the complex. However, several interesting observations were made concerning the stability toward reduction of certain cobalt complexes. Two new platinum(II) complexes were prepared, each containing one nitro group and a tridentate chelating agent. These are [Pt dien(NO_2)]Br and [Pt bamp(NO_2)]NO_3 (where dien = diethylenetriamine, bamp = 2,6-bis-(aminomethyl)-pyridine). Both of these compounds were found to give a polarographic wave in tenth molar perchloric acid which is four electrons high. The half-wave potential was about -0.6 volts versus the saturated calomel electrode. This is interpreted as a reduction of the coordinated nitro group to a hydroxylamine group. Suggestions are made concerning further confirmatory experiments.

Some Recent Developments in Fused Salt Chemistry

John P. Dismukes September 17, 1957

The design and operation of equipment and processes at temperatures from 100°C. to 1500°C.[and higher] necessitates a sound understanding of chemical reactions in molten media at high temperatures. In spite of numerous technical applications of high temperature chemistry in the fields of nuclear reactors, aircraft design, metallurgy, and synthesis, research still falls short of current needs. Three topics of interest will be treated in this seminar: [1] Metal-Metal Halide Systems [1-10], [2] Complex Ion Formation in Fused Melts [11-15] and [3] The Structure of Molten Silicates. [16-18]

Metal-Metal Halide Systems

Although the solubility of certain metals in their halides was noted as early as 1807, little systematic study of fused metal-metal halide systems was undertaken prior to 1940. In view of more complete phase diagrams of the alkali metal-metal halide systems published since 1954, [2-3] previous conclusions as to the nature of the interaction in these and other fused metal-metal halide media based on solubility data taken over smaller concentration and temperature ranges bear re-evaluation. The systems of Na,K,Cs,Ca,Sr,Ba,Al,Zn,Cd,Pb,Ag,Tl,Ce,Sb,Bi,Ga, and other metals with various of their respective halides [4-10] have been investigated, with much recent emphasis on subhalide formation.

It is characteristic of all these metal-metal halide systems that solidification produces an intimate mixture of the two components. Though it is difficult to visualize the formation of discreet, lower-valent cations even in the liquid state for the alkali and alkaline earth metals, the evidence for Cd[1], Bi[1], and Ga[1] is substantiated. [4,6,10] The compound originally proposed as CaCl has subsequently been identified as CaHCl. [1] The molten metal-metal halide phase has been characterized as a true solution in many cases where a marked depression [1-3] of the freezing point of the salt occurs on solution of metal; the earlier theory of colloid formation has been largely discarded. Observed depressions compare within an order of magnitude with those calculated from Raoult's Law.

The possible formation of slightly stable lower-valent cationic species in metal-metal halide melts has been correlated extensively with variations in solubility of the metal within a periodic group, with change in halide ion, with charge of the metal cation, polarizability of the metal cation, variations of solubility upon addition of foreign salts, and other properties. Because of insufficient data on such solution properties as electrical conductivity, density, viscosity, and the variation of these properties with temperature and composition, correlations of such empirical factors as "size and charge" with solubility alone probably do not constitute reliable proof of the existence of discreet subhalide species. Recent isolation of stable, solid, subhalide compounds of Bi[1], Cd[1], and Ga[1] from molten metal-metal halide melts by means of "acid stabilization" does, however,

favor the existence of lower-valent cations in these melts. Addition of $AlCl_3$ to the Bi-$BiCl_3$, Cd-$CdCl_2$, and Ga-$GaCl_2$ systems produces monovalent chloroaluminates. It is postulated that removal of halide ion by the acid(or complex forming) $AlCl_3$ shifts the equilibria in the above systems towards the formation of more basic monovalent Bi, Ga, and Cd cations.

$$BiCl_3 + 2Bi + 3AlCl_3 \rightarrow 3BiAlCl_4$$

$$CdCl_2 + Cd + 2AlCl_3 \rightarrow 2CdAlCl_4$$

$$GaCl_2 + Ga + 2AlCl_3 \rightarrow 2GaAlCl_4$$

The isolation of stable, solid BiCl[6] is also reported; the method of preparation is not given. Since the structure of $GaCl_2$ has been established as Ga(I)Ga(III)Cl_4, the formation of $GaAlCl_4$ is quite reasonable. Additional support for Cd(I) comes from electrical conductivity experiments[10]; a colored cationic species moves toward the cathode during the electrolysis of the Cd-$CdCl_2$ system. The diamagnetic character of the Cd-$CdCl_2$ system suggests the existence of Cd_2^{++} ion. The evidence for a unified theory of subhalide formation in molten metal-metal halide systems is considered sound enough by some investigators[6] to qualify the postulation of monovalent cations in such systems as Ce-$CeCl_3$, Sb-$SbCl_3$, and Zn-$ZnCl_2$, where no stable solid compounds have been isolated. Satisfactory interpretation of solubility in the alkali metal-metal halide systems, which are at present the most widely studied systems, must await further study of their physicochemical properties in the liquid state. Complete miscibility[1-3] in all proportions above a consolute temperature exists in the systems MX-M (where M=Na,Cs and X=F,Cl,Br,I) and KF-K. Explanations of solubility in these systems have been proposed recently in terms of the formation of diatomic molecules(e.g.K_2) in the liquid state and earlier in terms of the filling of vacant cationic sites in the liquid by metal atoms. The scarcity of data warrants much further study before definite conclusions are made.

Complex Ion Formation in Fused Systems

Several methods are being investigated currently to study complex ion formation in fused salts. Emphasis has centered mainly on chloride complexes of Zn(II), Pb(II), Cu(II), Co(II), and other cations whose chloride complexes are known to exist in aqueous solution.

Recent work on freezing point depressions in some fused salts (e.g. $NaNO_3$)[11-12] indicates excellent agreement with Raoult's Law. The depression of the freezing point of $NaNO_3$ by NaCl is linear up to 7 mole per cent NaCl(eutectic composition). At least twenty salts were studied in $NaNO_3$, and the agreement with Raoult's Law was good in each case. The freezing point depression constant for $NaNO_3$ is 15°. Common ions(Na^+ and NO_3^- in $NaNO_3$) were found to have no effect on the freezing point. As a consequence of the fact that strong electrolytes are completely dissociated in molten $NaNO_3$, some interesting conclusions as to the nature of $CdCl_2$, $ZnCl_2$, $PbCl_2$, and $CdBr_2$ in molten $NaNO_3$ follow from freezing point data on these systems. A considerable fraction of each of these

halides is present as covalent, undissociated molecules. Addition of ionic chlorides causes an elevation of the freezing point; this elevation is ascribed to a decrease in the number of solute particles due to complex ion($MCl_4^=$) formation. Additional support for chloride complex formation in fused nitrate media comes from a recent study of the ultraviolet and visible spectra of $CuCl_2$, $NiCl_2$, $CoCl_2$, and others in the fused $LiNO_3$-KNO_3 eutectic[14] (m.p. 132°C.), with and without the addition of KCl. In further study of the $LiNO_3$-KNO_3 eutectic it has been shown that solutions of Fe(III), Co(II), Ni(II), Cu(II), and UO_2(VI) (as their chlorides) may be adsorbed on a column of activated alumina at 150°C. and subsequently eluted with complex forming anions such as Cl^-, $SO_4^=$, or CN^-. Marked changes in the spectra of these metal ions take place on addition of Cl^-, $SO_4^=$, or CN^-.[15]

The Structure of Molten Silicates

Molten silicate chemistry is a field in which, until recently, there was little fundamental research compared with the large volume of applied industrial work. Studies of electrical conductivity, viscosity, density, and other fundamental properties[16-18] have established the ionic character of these fused media. These data have lead to a re-appraisal of liquid silicate structure, which for many years was considered similar in nature to that of fused SiO_2. On account of the scope of molten silicate chemistry, for the purposes of this seminar its inclusion serves mainly as an example where physical measurements have been successfully applied to the structure of molten liquids. The method of approach might well serve as a model for a more complete evaluation of molten metal-metal halide systems.

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INORGANIC FLUORINE CHEMISTRY

S. K. Madan September 24, 1957

A. Introduction

Modern developments in the descriptive inorganic chemistry of fluorine and its compounds have been the subject matter of numerous recent reviews (1-4). It is the objective of this presentation, therefore, to discuss briefly some of the physical properties of the fluorine molecule, the fluorine atom, and the fluoride ion, and, thereby show how an understanding of these properties can help in understanding of the chemistry of fluorine and its relationship to the other halogens.

B. Physical Characteristics of the Fluorine Molecule

a. Interatomic Distance: Electron diffraction (5) and the Raman spectroscopic methods (6) have led to the values 1.435 and 1.416 A°, respectively. The covalent radius of fluorine may be taken as 0.71A°. For chlorine, bromine, and iodine the covalent radii are 0.99, 1.14, and 1.33 A°, respectively, showing that the volume of a fluorine atom in the combined state is only 1/3 that of the chlorine atom and less than 1/6 that of the iodine atom.

b. Dissociation Energy: Older values for $D(F_2)$ were usually based on extrapolation of those for chlorine, bromine, and iodine (58.0, 46.1 and 36.1 k.cal, respectively), and were of the order of 60-70 k.cal. Recent workers have suggested that the true value is 37.0±8 k.cal.

1. Doescher (7) obtained a value for $D(F_2)$ at 25°C=37.4±0.4k.cal.
2. Wise (8) found $D(F_2)$=39.9±0.8 k.cal.
3. Barrow and Caunt (9) obtained $D(F_2)$=37.6±3.5 k.cal.

This low value is generally attributed to repulsion of non-bonding electrons in the F_2 molecule, but it has also been suggested that for chlorine, bromine, and iodine hybridization of p- and d- valence shell orbitals strengthens the bonding (10,11).

c. Thermodynamic Functions: These factors have been calculated (12) and reflect two important points: 1) Fluorine dissociates into atoms to a greater extent than chlorine at the same temperature. Since reactions of atomic fluorine are strongly exothermic the great activity of the element may be attributed to the weakness of the bond in F_2 molecule. 2) The standard entropies of molecular and atomic fluorine differ but little from those of molecular and atomic chlorine; differences between the two halogens are due to heat effects, i.e., to bond strengths rather than to entropy effects.

d. Ionization Potential: The high value of 420 kcal/g-ion suggests that the solvated fluoronium ion is unlikely to be encountered in chemical investigation. There is, in fact, at the present time no evidence of any kind for the existence of the positive fluorine ion.

e. Electron Affinity: A Born-Haber cycle calculation for fluorine leads to a value for E(F)=84±2 k cal/g-atom (13), which is intermediate between those for chlorine and bromine. It was first pointed out by Evans and co-workers (10) that the quantity conforms well to the low value of $D(F_2)$.

C. The Valency of Fluorine Atom

The electronic configuration assigned to the fluorine atom is $1s^2 2s^2 2p^5$. Expansion of the valency shell beyond $2s^2 2p^6$ is improbable. With the possible exception of the difluorides and trifluorides of the alkali metals (14), such as RbF_3, which is obtained by the action of fluorine on rubidium chloride at 150°C, this generalization seems valid for all fluorine compounds.

D. Physical Characteristics of the Fluoride Ion

a. Ionic Radius: The radii of the halide ions are F^-=1.36; Cl^-=1.81; Br^-=1.95; and I^-=2.16A°. The fluoride and oxide ions are of almost identical size [$r(O^{2-})$=1.40A°]. This is believed to account for the similarity in structures which is often found among oxides and fluorides of the same formula type (e.g., MgO and NaF). Fluorides and chlorides of the same metals, however, often have quite different structures. Thus, CdF_2 and HgF_2 both crystallize with the fluorite structure, $CdCl_2$ crystallizes in a layer lattice in which Cd^{+2} ion has coordination number six, and $HgCl_2$ exists as a molecular lattice.

b. The Standard Potential of the Fluorine-Fluoride Ion Electrode: An indirect calculation of E^0 for the fluorine-fluoride electrode from related thermochemical data leads to value of +2.8 v; for the chlorine-chloride couple it is +1.36 v. The figure for fluorine shows that it is the most powerful oxidizing agent known and explains why the element can be prepared only by thermal decomposition of a few higher fluorides or electrolysis of solutions of ions of fluorides in media in which no other anion is present.

E. Chemical Characteristics of Inorganic Fluorine Compounds

a. Dissociation of HF in aqueous solution: The large dipole moment of HF shows that the H-F bond is strongly polar. The chain structure of solid hydrogen fluoride (15) arises from dipole-dipole attraction. In dilute aqueous solutions, however, HF is a much weaker acid than the other hydrogen halides. The general process of ionization may be shown as taking place in the following stages:

$$HX_{(g)} \rightarrow H_{(g)} + X\cdot_{(g)} \rightarrow H^+_{(g)} + X^{-(aq)}_{(g)} \rightarrow H^+_{(aq)} + X^-_{(aq)}$$

The stages involving the conversion of a hydrogen atom into a solvated proton are the same for all acids, and only four variables have to be considered.

1. Energy of solution of the undissociated molecule
2. The dissociation energy of the H-X bond
3. The electron affinity of X
4. Solvation energy of X^-

In case of HF, factor 2 is most important since bond energies vary as follows: HF=135; HCl=103; HBr=87; HI=71 k cal. In more concentrated solutions (5-15M), ionization into H_3O^+ and HF_2^-, $H_2F_3^-$, and $H_3F_4^-$ takes place, and HF becomes a strong acid. The formation of these stable acid anions in liquid hydrogen fluoride accounts for the greater proton-donating (i.e., acidic properties) of this solvent.

b. Hydrogen Bonding in Fluorine Compounds: Since fluorine is the most electronegative element, it will take part in hydrogen bond formation. Some of the best known instances of this phenomenon do, in fact, involve covalently bonded fluorine or the fluoride ion. The strength of the bonding in HF_2^- ion is also remarkable. The fluorine-fluorine distance in this ion is only 2.26 A^0. A neutron diffraction study (16) of potassium hydrogen difluoride shows that the hydrogen is in the middle of the linear ion. The structure of ammonium fluoride also differs from the other halides; in this salt each nitrogen atom forms four N-H bonds of length 2.69 A^0 to the four fluorides ions arranged tetrahedrally around it (17).

c. Fluorides of Non-Metals: The stability of non-metallic fluorides is often cited as a remarkable feature of fluorine chemistry. It is not always realized that these compounds are not particularly stable thermodynamically.

A satisfactory discussion of this topic must involve consideration of energy changes involved. The formation of sulfur hexafluoride may be represented as taking place in the following stages:

S_8(solid)→S(gas; ground state $3s^23p^4$)→S(gas; valency state $3s^13p^33d^2$)

$3F_2$(gas)→6F(gas) ⟶ SF_6(gas)

d. Fluorides of Metals: Generally speaking, two features distinguish the chemistry of metallic fluorides: 1. Many metals show their highest oxidation states in the fluoride salts, e.g., Co in CoF_3; Ag in AgF_2; Bi in BiF_5; Tb in TbF_4; Rh in RhF_4. 2. Many fluorides in these higher oxidation states are salt-like, whereas the corresponding chlorides are not, e.g., AuF_3, PbF_4, TlF_3. Many of transition metal fluorides (e.g., MoF_6, UF_6, OsF_8) are volatile and generally resemble the fluorides of non-metallic elements.

e. Complex-Fluorides and Fluoro-acids: The relatively small size of the anion plays an important role among complex fluorides. By use of elemental fluorine (18) and of bromine trifluoride, an interesting non-aqueous solvent and fluorinating agent (19,20), many new complexes involving unusual oxidation states have been obtained (e.g., Cs_2CoF_6, K_2NiF_6, K_3CuF_6). Most of these compounds are hydrolyzed to oxides by water.

All complex fluoro-acids are strong acids. The univalency of fluorine provides a simple and convincing explanation of this fact in the case of fluoroboric acid, where the formulation of the undissociated molecule HBF_4 is impossible without involving quinquevalent boron or bivalent fluorine.

F. Conclusion

Fluorine owes its remarkable chemical behavior 1) to the smallness of the fluorine atom and of the fluoride ion, 2) the restriction to an octet of electrons, and 3) the weakness of the bond in the F_2 molecule. It would not be realistic to suggest that our knowledge of the chemistry of the element is complete, but with the help of physical methods of investigation a deeper insight into its properties is rapidly becoming possible.

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THE ROLE OF π BONDS IN COMPLEX FORMATION

N. Koertge October 1, 1957

I. Introduction

π-Bonds are formed from pure or hybrid atomic orbitals whose component of angular momentum around the bond axis is equal to one (1). Although they actually constitute molecular orbitals and are used to describe such phenomena as paramagnetic resonance absorption (49), proponents of the valence-bond picture utilize π-bonds to supplement their theory, e.g., Pauling Electroneutrality Principle (2). π-Bond also provides an explanation for some discrepancies between actual relative stabilities and those predicted from crystal field considerations alone (33).

II. Theoretical Considerations

A. Directional Suitability of Orbitals

The following table lists those orbitals whose angular dependence renders them potential participants in π-bonding (3).

Configuration	σ-bonds	π bonds	δ-bonds
Tetrahedral	s, p_x, p_y, p_z.	d_{xz}, d_{yz}.	--
Tetragonal planar	$d_{x^2-y^2}, s, p_x, p_y$.	$d_{xy}, d_{xz}, d_{yz}, d_{z^2}(?), p_z$.	d_{xz}, d_{yz}.
Octahedral	$d_{x^2-y^2}, d_{z^2}, s, p_x, p_y, p_z$.	d_{xy}, d_{xz}, d_{yz}.	d_{xz}, d_{yz}, d_{xy}.

On the ligand, p_z, p_x or p_y, d_{xy}, d_{xz}, d_{yz} as well as molecular orbitals (cf. olefins) may be used. Exact directional properties of p orbitals, which are cylindrically symmetric, are unimportant but the orientation and symmetry of d orbitals is critical (7), e.g., in tetrahedral complexes only two metal d orbitals could be used and the angle between them is too small for maximum bond strength. In general, use of either a metal or ligand dp hybrid leads to stronger bonding. To avoid interaction, π bonds should be orthogonal to the σ-bonds in the molecule.

B. Energy Considerations

The two atomic orbitals which comprise the π molecular orbital must be of similar energy and appropriate size (5). Their principle quantum numbers, the inductive effect of ligands (2), the possibilities of conjugation (7), the polarity of the σ-bond connecting metal and ligand (6), as well as the charge on the metal, all influence the energetic feasability of forming a particular π bond. Calculated overlap integrals, though the values are very dependent on the effective nuclear charge, give an approximate indication of the relative importance of π bonding in various compounds (7):

Compound	S_π	Compound	S_π	S_δ
C_C (olefin)	0.27	$Pt-PR_3$	0.06	0.13
$Fe(CN)_6^{-4}$	0.20	$Pt-PCl_3$	0.11	0.15
$Fe(CN)_6^{-3}$	0.17	$Pt-PF_3$	0.30	0.16
$Ni(CN)_4^{-2}$	0.11 (or 0.20 if dp)			

III. Evidence for π-Bonding

A. Relative Stabilities of Complexes

If the only consideration were strength of the σ-bond, the stabilities of a series of metal complexes should increase with increasing basicity of the ligand. Many exceptions may be conveniently explained in terms of π-bonding:

1) Fe(II) complexes with heterocyclic amines are diamagnetic and more stable than the paramagnetic ones formed with aliphatic amines (9,19).

2) Pt(II) reacts with PF_3 but not NF_3 although the latter acts as a better donor towards BF_3 (9).

3) In $GaMe_3 \cdot LR_2$ the following order of stability holds:

   L = O > Se > S = Te while the analagous Al compounds show the normal order O>S>Se>Te (15).

4) PR_3, AsR_3 and SbR_3 form more stable complexes with Pt(II) than do amines (37).

5) A Ni(II) complex containing dipyridyl can be resolved but the corresponding one with ethylenediamine cannot (5).

6) Substitution of F for R in $[(PR_3)_2\ PtCl_2]$ increases stability (34).

7) The stability of most halogen complexes lies in the order:

   F>> Cl>Br>I but with Pt(II), Cl>F as is also $SR_2 > OR_2$ (56). Likewise, in general complex stability should increase with the acceptor character of the metal. However:

1) CN^-, CO, NO complex Ag, Cu, transition and even IIB metals but not Al or other metals containing no penultimate d electrons (4).

2) The above-mentioned complexes are more stable than those with Cl, Br or other ligands containing no empty valence p_π orbitals (4).

3) Tl and In compounds with SeH_2 and SeH_2 are more stable than the corresponding Ga and Al complexes (16).

4) Diarsine will not form stable compounds with metals having no d_π electrons, e.g., Cr(III) and Mn(II) (9).

The formation of pentacovalent Pd and Au diarsine complexes may be due to the positive charge on the metal resulting from two metal-ligand dative π-bonds (28, 45). A similar explanation may be given for the greater stability of certain cis-isomers, e.g., cis-$[PtCl_2(PF_3)_2]$ has been prepared but not the trans (4, 39).

B. Evidence From Physical Measurements

The above body of chemical evidence is augmented by physical measurements that give indirectly an approximation of the amount of π-bonding occurring:

1) The heat content of cis-$[(PMe_3)_2PtCl_2]$ where two π-bonds are possible is 5-10 kcal/mole greater than that of the trans-isomer in which there is a possibility of only one double bond (38).

2) Dipole moments of Pt-L bonds are unusually low when the ligand is capable of forming π-bonds (39, 41).

3) Bond lengths of carbonyls indicate partial double bond character (2, 23, 14).

4) Comparison of redox potentials may give an indication of the relative extent of π-bonding in certain complexes (41).

5) Attempts have been made to relate the color of certain Fe(II) organo-nitrogen complexes in terms of a π-bonded chromophore (18, 9).

6) X-ray crystal studies showing the position and rigidity of ligands give hint of π-bond formation (17, 26).

7) Magnetic moments show the Ni(II) complex with diarsine is covalent while the dipyridyl is ionic (43).

8) Trends in the acid strength of p-$H_3MC_6H_4COOH$ where M = C, Si, Ge, Sn do not parallel those of the electronegativity of M (40).

9) Values of the force constants of the C-O bond in substituted nickel carbonyls indicate the relative amount of π-bonding occurring (43, 23, 25).

10) Frequency of the N-H stretch in trans-$[L\text{-amine } PtCl_2]$ complexes was used to investigate the relationship between strength of Pt-N bond and the π-bonding ability of L (42, 11).

A new theory concerning the causes of trans-directing influence resulted.

11) Paramagnetic resonance data are interpreted as indicating considerable π-bonding in $IrCl_6$ = (20, 51, 53) /and $Cu(acac)_2$ (21, 54). Weak π-bonds could be postulated for certain transition metal hydrates also (49, 52), although there are alternate explanations for the nature of the fine structure.

IV. Other Explanations of π-Bonding

A. Mechanism of Trans-Directing Influence

Chatt suggests that the older, essentially electrostatic pictures (4, 30, 50) be replaced by a process in which electrons are removed through π-bonding from the metal d orbital which is attached by the incoming ligand in the transition state (12, 13). This concept demands that trans substitutions occur rapidly and by a S_n2 mechanism in contrast to the slow S_n1 Cis replacement reactions. Available experimental evidence substantiates the theory (42, 46).

B. Platinum-Olefin Complexes

The old ethylidene structure (22) and the suggestion that Pt(IV) is involved have been discarded due to IR and chemical evidence to the contrary(32). Many of the chemical and physical properties of these compounds (27, 31, 10, 23, 36) are best explained at present by the π-bonded structure proffered by Dewar (55).

V. Conclusion

The limitations of using double bonds must clearly be realized. The stability of complexes is dependent on many factors (6, 8) of which π-bonding is only one. The existence of Mo and Cr complexes, for example, indicates that double bonding is not indispensible (4). Recent extension of the theory to include halogen and boron compounds (35, 24, 6) may not be justified.

There is a great need for determinations of proton affinities, heats of formation, force constants and other quantitative data (6). IR, charge-transfer, and paramagnetic absorption spectra may well provide the means to investigate bonding in more detail. However, the primary importance of chemical investigations of the trends in the behavior and properties of metal complexes must not be overlooked.

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THESIS ABSTRACT

THE PHOSPHORUS SULFIDES

Anthony R. Pitochelli October, 1957

All the phosphorus sulfides show an infrared spectrum in which both the wavelength and shape of the minima are characteristic for each compound. The x-ray diffraction patterns of the sulfides of phosphorus are also sufficiently characteristic to be useful for purposes of identification.

The investigation of the effect of time, light and iodine catalyst on the reaction occurring between white phosphorus and sulfur in refluxing xylene showed that prolonged refluxing leads to the formation of the decasulfide instead of the heptasulfide, both in the presence and absence of light and iodine. A reaction mechanism is suggested to explain this result.

The claim that the high temperature reaction between trisulfide and sulfur dissolved in carbon disulfide leads to the formation of P_2S_4 and P_8S_{11} was found to be incorrect. The products actually isolated were P_4S_5 and P_4S_7. Also found fallacious was the claim that the product of reaction between phosphorus trichloride and liquid hydrogen sulfide is P_2S_3. This work has demonstrated that the product is actually a mixture consisting essentially of P_4S_5 and P_4S_7.

Solubility tests uncovered no solvent which dissolved sufficient amounts of the higher sulfides of phosphorus at room temperature to give solutions useful for the determination of nuclear magnetic resonance spectra.

A method developed for the rapid oxidation of the phosphorus sulfides proved useful only when the sulfur content of a sample is being determined. The results of phosphorus analyses were low.

A carbon disulfide solution of P_4S_5 displays no optical activity. This constitutes negative evidence for the existence of mirror images of this substance.

ELECTRODEPOSITION FROM AQUEOUS SOLUTIONS

Ronald D. Archer October 8, 1957

Almost all solutions successfully used for electrodeposition of metals seem to contain "outer orbital" complex ions[1-3]. However, certain "inner orbital" complexes have also been electrolized, although these solutions give deposits only with low current efficiencies and high activation overpotentials[1-4]. The behavior of both types of solutions has been explained thermodynamically[1-3].

Early Theories

Electrodeposition is an area of electrochemistry in which theory has lagged behind practice. For example, silver has been deposited from solutions in which the metal is complexed as an anion for about 120 years but the theories used to interpret actual cathode processes are still speculatory. The reluctance to picture a negative ion being reduced at a negative electrode was a stumbling block to early theorists. To avoid this the following theories were advanced:

1) The Alkali Metal Reduction Mechanism
2) Nascent Hydrogen Mechanism
3) Dissociation Hypothesis
4) Intermediate Complex Cation Theory

Although the alkali metal reduction mechanism has been discarded, the others may still be of importance in certain deposition processes. In fact, partial dissociation of $[Cd(CN)_4]^{2-}$ to $[Cd(CN)_3]^-$ before discharge of Cd has recently been proven[5].

None of these theories is ordinarily necessary because

a) negatively charged ions are attracted and bound to other ions which already have negative charges[3];
b) electrical transport is very small or negligible in bringing the ions to the cathode[3,6];
c) certain complex anions can be shown to undergo direct reduction (for example, $[Fe(CN)_6]^{3-}$ can be reduced to the divalent, monovalent, and zerovalent states under proper conditions[3]).

Electronic Structure and Lability

Complex ions have been classified on the basis of electronic configuration by Taube[7] as either "inner orbital" or "outer orbital". The inner orbital complexes are those in which the hybridized orbitals include d orbitals of a lower principle quantum number than the hybridized s and p orbitals. For a hexaccordinated complex this can be designated as d^2sp^3. Outer orbital complexes are those in which the hybridized orbitals are of the same principle quantum number; e.g., sp^3d^2.

A correlation between ion type and the ease of substitution has been shown[7]. The outer orbital complexes display a very rapid

exchange rate of coordinated groups with the solvent or are classed as "labile". The inner orbital complexes of hexacoordinated complexes are relatively inert to substitution except in the cases in which an unoccupied inner d orbital or a p orbital is available after hybridization.

Electronic Structure and Deposition

Although specific deposition processes have been studied by numerous investigators, the few attempts to categorize the known facts have usually been too involved and empirical to be worthwhile. The one exception is that of Lyons[1-4,8,9], who used Taube's classification of complexes as a tool to systemize deposition processes.

As far as electronic structure and deposition are concerned, a very worthwhile relationship was noted. In general, outer orbital complexes with their relatively weak bonds are deposited rather easily. Inner orbital complexes are held together by stronger bonds; it is therefore more difficult to remove coordinated groups, as is required for deposition. If the energy required to break the bonds exceeds that needed to release hydrogen, no metal will be deposited. The cases in which deposits are formed (several platinum group complexes) are characterized by low efficiencies and high activation overpotentials. Other cases of "flash" deposits have been noted. The table which follows illustrates this correlation.

TABLE

Classification of the Metal Complexes according to Electronic Structure and Character of Electrodeposition.

Inner Orbital Complexes

<u>No deposits obtained</u>: All complexes of Ti, Zr, Hf, V, Nb, Ta; most complexes of Cr, Mo, W; cyano complexes of Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt; o-phenanthroline complexes of Fe, Co, Ni, Cu, Rh, Ir, and other platinum metals; α, α'-bipyridine complexes of Fe, Co, Ni, Rh, Ir, and other platinum metals.

<u>Deposits obtained only as amalgams</u>: Tetracyano nickelate.

<u>Deposits obtained at low current efficiencies and high activation overpotentials</u>: Many complexes of the platinum group.

<u>Deposits obtained at high current efficiencies and low activation overpotentials</u>: None.

Outer Orbital Complexes

<u>No deposits obtained</u>: Complexes of Al, Be, Mg.

<u>Deposits obtained only as amalgams</u>: Complexes of the alkali metals, Ca, Sr, Ba; probably Sc, Y, lanthanide metals.

<u>Deposits obtained at low current efficiencies and high activation overpotentials</u>: None.

<u>Deposits obtained at high current efficiencies and low activation overpotentials:</u> Aquo and chloro complexes of Mn, Fe (II), Co (II), Ni, Cu (II), Zn, Cd, Hg, Ga, In, Tl, Pb, Sn; pyrophosphate complexes of Cu, Zn, Cd, and Sn; ammino complexes of Ni, Cu, Ag, Zn, Cd; o-phenanthrolino complexes of Zn and Cd; thiosulfate complexes of Cu and Ag; iodo complexes of Ag, Cd, and Hg; thiostannate; cyano complexes of Cu, Ag, Au, Zn, Cd, Hg, Tl, and Ir; hydroxo complexes of Zn and Sn; and others.

Notes:

1) Current efficiencies are considered high if greater than 50%.

2) Activation potentials are considered high if greater than 0.05 volts.

3) Cr and Co are deposited from certain ions which appear to be inner orbital complexes, but intermediate steps enter into the processes.

Note that there is a greater correlation here than in the case of substitution reactions for which the system of inner and outer orbitals was formulated as being helpful. For dsp^2 structures, substitution reactions are rapid even though these are inner orbital ions. This is not so in the case of electrodeposition; the hybridized inner d orbital is too stable to allow dissociation. The sp^3 hybrids of Zn, Cd, and Hg deposit readily, so it is likely that dissociation occurs easily as well as addition, (the view of Taube[7] with regard to sp^3 substitution reactions). In addition, hexa-coordinated inner orbital complexes with vacant stable inner d orbitals fail to deposit but do enter into substitution reactions giving even greater generality to Lyons' theory.

The theory does have its limitations. Many platinum group inner orbital complexes can be deposited (although only at low efficiencies and high activation overpotentials). Many other inner orbital complexes give "flash" deposits. Further clarification regarding the deposition of alloys from solutions which contain inner orbital complexes also seems necessary. Suggestions include heteronuclear complexes and lower free energy of the metal when alloyed[4]. Another serious problem is the lack of knowledge concerning the actual species being deposited at cathodes.

Vlček[10,11] has stated that the rules set forth here are oversimplified and has deduced several rules that seemingly hold for all cathode processes. Even with its exceptions, Lyons' theory seems to be of general utility, particularly at solid electrodes. Certain copper complexes were suggested by this theory as being outer orbital even though they have a square planar configuration. A recent infrared study[12] has substantiated the fact that one of these, bis-(glyoxino)-copper(II) monohydrate, is definitely outer orbital[4]. Further use of Lyons' theory regarding electrode processes has been recommended as a means of clarifying the confusion which exists about these processes[13].

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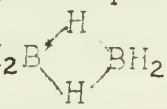
Addition Compounds of the Hydrides of Boron

Bruce R. Karstetter

October 15, 1957

A. Introduction

"The longstanding puzzle of the structure of diborane (B_2H_6) implied a need for an extensive experimental study of its chemical character and consequences, such as to supply a background of information which would be intelligible in terms of the structural situation. During the period of slowly developing recognition of the bridge structure  (in which four electrons are assumed to be shared among four B-2sp^3 and two H-1s orbitals), it became more and more evident that a great majority of the unusual reactions of diborane could be explained best as processes in which the bridge system is broken to supply the borine radical, BH_3. This group, having only a sextet of valence electrons, acts as an electron-acceptor in the formation of many BH_3 complexes, wherein the bonding situation conforms to the Lewis electron-octet theory of covalence. The general result of such complex formation is a large field analogous to organic chemistry but very different in many of its rules of behavior." (1).

Many of the better-known higher boranes (B_4H_{10}, B_5H_9, B_5H_{11}, and $B_{10}H_{14}$) are also good sources of the BH_3 group. The structures of these compounds are such that some boron atoms always are adjacent to three hydrogen atoms, so that the extraction of BH_3 groups merely require the breaking of a three center bridge bond by a strong enough base.

McCoy and Bauer (2,3) have carefully studied the dissociation of diborane:

$$B_2H_6\ (g) \rightleftharpoons 2BH_3(g)$$

By a process of thermochemical extrapolation they have estimated the value of the bridge dissociation to be 28.4$\pm$2 kcal/mole. The ΔH_f^o (300°K) for BH_3 is 18$\pm$1 kcal and the average bond dissociation energy for B-H is 93.1 kcal. From this, they conclude that the relative instability of the boron hydrides is not due to low bond dissociation energies, but to the presence of low energy barriers for dissociation to give highly reactive units.

B. General Behavior of Borine Complexes

Borine complexes are readily formed by reacting diborane with the corresponding base, and their stability, relative to the reverse reaction, is roughly correlated with the strength of the bases.

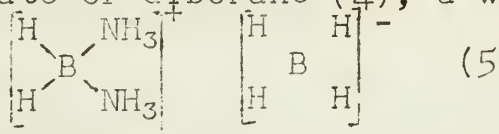
If the donor atom has a proton, this proton becomes more acidic as a result of the formation of the complex, while the B-H bonds become more reactive in the sense of supplying hydride (H^-) units. Thus, many of these complexes readily evolve hydrogen through a proton plus hydride combination, and often the intermediate borine complex is too unstable to be isolated.

Some borine complexes undergo an internal hydride ion shift to a position of lesser reactivity. The methylcyanide borine complex shifts two hydride ions to the nearest carbon atom to form (CH_3CH_2NBH) units in polymer form.

The varying rates of these hydridic reactions must depend upon two primary factors: the availability or reactivity of a proton or other hydride-acceptor, and the ease of activation of the B-H bond toward hydride activity. The more thorough the envolvement of the base electrons with boron the more hydridic in character the B-H bond will be. On the other hand, substitution of an electron withdrawing group like chlorine on the boron atom will decrease the hydridic character of the B-H bond.

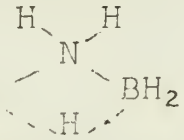
C. The Ammonia Chemistry of Diborane

A carefully controlled reaction between diborane and solid ammonia at -120° gives the diammoniate of diborane (4), a white solid, which is now known to be the salt



(5).

When the diammoniate is treated with an excess of diborane at 90°, the product is aminodiborane, B_2H_7N (6), the structure of which has been shown to be

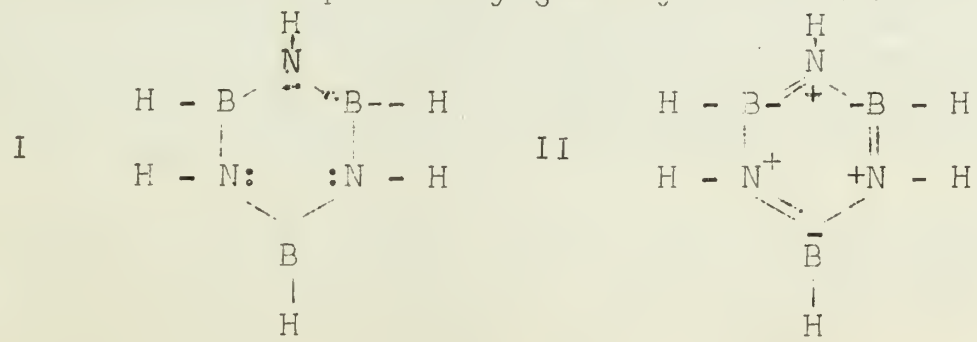


(1). Aminodiborance is very unstable and converts to diborane and a polymeric $(H_2NBH_2)_x$ which spontaneously loses hydrogen to form still more polymeric material (1).

The N- alkyl derivatives, like the N- dimethyl compound, $(CH_3)_2NB_2H_5$ which can be obtained quantitatively from $(CH_3)_2NBH_2$ and diborane, are more stable (7). The stability of the N- dimethyl compound implies the existence of many other N- alkylaminodiboranes, and even ring-aminodiboranes (e.g. $C_4H_8NB_2H_5$), several of which have been made (1).

The stability of an aminodiborane depends upon two main factors: the electron-donor bonding power which the substituted nitrogen can exert and the relative stability of the R_2NBH_2 unit, either as a polymer or as an internally-pi-bonded unit (1).

Diborane diammoniate, when heated suddenly to 200° in a closed tube will give borazole ($B_3N_3H_6$), often called the benzene of inorganic chemistry. There are some similarities in types of reactions and in structure which partially justify the name.



The unshared pairs of electrons on the nitrogen atoms in I can be donated to the electron deficient boron atoms, giving a pseudoaromatic system with π-bonding between the nitrogen and boron atoms (II). The comparison between borazole and benzene should not be carried too far, however, because of the basic difference between the B-N and C-C linkage. The bonding in benzene involves atoms of the same element while that of borazole involves atoms of differing electronegativity and, therefore, the electron cloud representing the bond is not symmetrical. Consequently, the boron-nitrogen bonds should be broken more readily than the carbon-carbon bonds and, in general, this is true.

Various N- substituted borazoles can be prepared by the use of amines, and B- substituted derivatives result from the use of substituted diboranes or by treating the ring compound with a trialkylboron at elevated temperatures.

D. Phosphine-Borine Chemistry

Development of aminoboron chemistry created much interest in the possibility of similar phosphino- and arsino-boron compounds. A study was made of the reaction between diborane and phosphine at -110^{0} (8) but, although the product had the composition $B_2H_6 \cdot 2PH_3$, it was not stable like the diborane diammoniate. Stone (9) suggests that the structure is probably $H_3\overset{+}{P} \cdot \overline{B}H_3$.

Burg, Wagner and Stone (10,11) have made a comprehensive study of boron-phosphorous bonding. Dimethylphosphine forms the expected addition compound, $Me_2PH \cdot BH_3$, with diborane below room temperature. Prolonged heating of this compound at 150^{0} yields an extremely stable and chemically resistant polymer of $(Me_2P \cdot BH_2)_x$ as the trimer, tetramer, and a trace of high polymer. Although they contain B-H bonds these polymers are exceedingly resistant to acid or base hydrolysis, and they can be recrystallized from organic solvents in the open air.

Burg and Wagner (10) suggest that these polymers are ring compounds, the structure of $(Me_2P \cdot BH_2)_3$ being based on a $(P-B)_3$ hexa-atomic ring, while the tetramer would have an octa-atomic ring. This structure for the trimer has been confirmed by x-ray diffraction studies (9).

Ring structures do not account for the inert character, however, which has been explained in terms of weak but multiple $B \rightarrow P$ π bonding using hybridized d-orbitals of phosphorous and a contribution of electron density from the B-H linkages (10,11). Thus, the electron density on hydrogen would be reduced, rendering the B-H bonds less susceptible to attack by protonic reagents. Such use of the B-H bonding electrons would tend to compensate the formal charge distribution brought about by the $P \rightarrow B$ σ bonding, and the bonding would be much stronger than in $Me_2N \cdot BH_2$ since nitrogen has no such abundance of orbitals available for bonding as phosphorous.

The effects of two methyl groups replacing the hydrogen in $Me_2N \cdot BH_2$ are to strengthen the B-P π bonding and weaken the σ bonding. The two effects approximately compensate each other so that $Me_2N \cdot BH_2$ and $Me_2N \cdot BMe_2$ are almost equally inert.

E. The Thioborines

Methylated sulfur will form borine complexes, and it is possible to obtain a mixture of $(CH_3SBH_2)_x$ polymers by loss of hydrogen from $CH_3SH \cdot BH_3$. The process occurs fairly well below room temperature, but as the product is formed the remaining $CH_3SH \cdot BH_3$ units become separately buried in the mass, and the rates of dissociation and loss of hydrogen greatly decrease, so that completion of the protolysis requires room temperature. Thus, both the dissociation and the protolysis would seem to require contact between two molecules of the complex, rather than occurring within each.

Graham and Stone (12) have studied the relative stabilities of complexes between BH_3 and oxygen, sulfur and selenium compounds. The order was found to be S > Se > O.

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THE ACIDITY FUNCTION AND ITS APPLICATION

R. Latham

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Introduction

When a simple basic indicator is used to measure the acidity of a solution, it was pointed out by Hammett (1,2) that one is not measuring the hydrogen ion activity which is the usual measure of acidity. Instead, what is being measured is the tendency for the acids present in the particular environment under study to transfer protons to the neutral base used as the indicator. As the solution becomes increasingly more dilute, the pH is an adequate measure of the acidity. But the true acidic nature of the solution increases quite rapidly as the concentration of acid is increased and pH loses its significance.

Hammett's H_o Acidity Function

For indicators reacting in the following manner:

$$B + H^+ \rightleftharpoons BH^+$$

Hammett (3) quantitatively defines an acidity function H_o.

$$H_o = pK_{BH^+} - \log {}^{C_{BH^+}}/_{C_B} \qquad [1]$$

where ${}^{C_{BH^+}}/_{C_B}$ is the conc. ratio of the indicator in its two different forms and pK_{BH^+} is the thermodynamic ionization constant of the base's conjugate acid in terms of molar concentrations.

Since $K_{BH^+} = \frac{a_B a_{H^+}}{a_{BH^+}}$ and $a = fc$ the H_o acidity function can be rewritten:

$$H_o = -\log a_{H^+} \frac{f_B}{f_{BH^+}} \qquad [2].$$

Certain assumptions have been made in deriving such an equation as [1].

1. The relative strength of two bases of the same charge type is assumed to be independent of the medium in which they are compared.
2. The ratio ${}^{f_B}/_{f_{BH^+}}$ is assumed to be constant for all indicators of the same charge type.
3. The ratio ${}^{f_B}/_{f_{BH^+}}$ is assumed to be independent of the solvent.

Measurement of the quantity C_{BH^+}/C_B in equation [1] is accomplished with either an optical colorimeter or more recently with photoelectric spectrophotometers. pK_{BH^+} is measured by the following comparison method: (3)

Since $pK_{BH^+} = \log \frac{C_{BH^+}}{C_B C_{H^+}} + \log \frac{f_{BH^+}}{f_B f_{H^+}}$ [3] the difference between the pK_{BH^+} of two indicator bases of slightly different pK_{BH^+} can be defined.

$$pK_{CH^+} - pK_{BH^+} = \log \frac{C_{CH^+}}{C_C} - \log \frac{C_{BH^+}}{C_B} = \log \frac{f_C f_{BH^+}}{f_{CH^+} f_B} \quad [4]$$

Taking assumption 2 above as valid, the term $-\log \frac{f_C f_{BH^+}}{f_{CH^+} f_B}$ becomes negligible for aqueous solutions and presumably for other solvents of high dielectric constant. If pK_{BH^+} is already known, and the concentrations of the various species can be measured, pK_{CH^+} can be calculated. The validity of the above assumptions has been demonstrated by consistent pK_{BH^+} measurements for an indicator in various solvent systems and by the general parallelism of the logarithm of indicator ionization ratios over the entire range of H_2SO_4 concentrations.

Other acidity functions have been defined, such as H_+ and H_-, where the subscript refers to the charge on the indicator base, but little work has been done to characterize such acidity functions.

Media In Which The Acidity Function Has Been Determined.

The acidity functions for solutions of all the common strong acids and several "weak" ones in H_2O have been determined over a wide range of molarities. The H_0 acidity function for 0-100% H_2SO_4 solution has been determined by Hammett and Deyrup (2). This was extended to 107% H_2SO_4 (4,5). Other acids used have been hydrochloric (6), phosphoric (7), hydrofluoric (8), nitric (2), perchloric (2), perchloric acid-sodium perchlorate mixtures (9), dichloroacetic acid (10), potassium hydrogen sulfate (10), trichloroacetic acid(11), and trifluoroacetic acid (11). Interesting structural relationships have been discussed by some authors for various solutions. A recent paper (11a) discusses the structure of HF with relation to the acidity function. As the HF concentration increases up to 50% HF, the acidity increases due to the formation of HF_2^-, $H_2F_3^-$, and longer chains. After the 1:1 point is reached, the species H_2F^+ appears.

Non-aqueous and mixed solvents have also been used as media for the determination of the H_0 acidity function of various acids. The resulting acidities are automatically referred to the dilute aqueous reference state. Using formic acid as a solvent, the acidities of solutions of benzene-sulfonic acid, sulfuric acid, sodium formate, and aniline were determined (12). Ether-formic acid mixed solvents were also used as media (13). H_0 values were determined in anhydrous acetic acid for H_2SO_4 (14) and $HClO_4$ (15). Urea, antipyrine, and buffer mixtures with H_2SO_4 have also been used as solutes in anhydrous acetic acid (16). Acidity function values of $HClO_4$ in acetic acid-water mixtures have been measured (17). As H_2O is added, the H_0 value

decreases sharply. Thus, for 0.001 M $HClO_4$ in HAc, H_0 decreases from -1.00 to +1.93 as the water content increases from 0 to 5%. The H_0 value for H_2SO_4 in HAc-H_2O solutions has been measured (18). Measurement of H_0 values for .075 M perchloric acid in an acetic acid-acetic anhydride medium (19) indicate that acidity increases with increasing anhydride concentration. However, these results have been questioned. Solutions of HCl in ethanol, acetone, and dioxane (20) and of HCl in water-ethanol, -acetone, and -dioxane solutions (21) have been investigated. HCl acts as a strong acid in ETOH and acetone, and as a weak acid in dioxane. Using nitromethane as a solvent, the H_0 acidity function was determined for H_2SO_4, HCl, $MeSO_3H$, and a buffer solution of H_2SO_4 with pyridine (22). Hammett's acidity function was also determined in aqueous hydrazine solutions, the acidity being outside the pH range of H_2O (23).

The Use of the Acidity Function in Kinetic Studies

The best example of the utility of the H_0 acidity function concept lies in its relation to the rates of certain chemical reactions. It has been shown mathematically and experimentally (24) that for acid catalyzed reactions in concentrated acid solution, postulated reaction mechanisms can be related to the H_0 acidity function or the $[H_3O^+]$ hydronium ion concentration.

1. For acid-catalyzed reactions in which the rate-controlling step is a first order reaction of the conjugate acid of the reactant, the log k is proportional to the acidity function H_0. The mechanism for such a case might include the following:

$$L + H^+ \rightleftharpoons LH^+ \qquad \text{Equilibrium}$$
$$LH^+ \rightarrow M^+ \rightarrow \text{Products} \qquad \text{Rate Controlling}$$

The activated complex M^+ differs from the reactant only by the addition of a proton.

2. For acid-catalyzed reactions in which the rate-controlling step involves the addition of a water molecule to the conjugate acid of the reactant, a linear relationship is observed between the rate and the hydronium ion concentration. A mechanism for case 2 may be set up as follows:

$$L + H^+ \rightleftharpoons LH^+ \qquad \text{Equilibrium}$$
$$LH^+ + H_2O \rightarrow M^+ \rightarrow \text{Products} \qquad \text{Rate Controlling}$$

The activated complex differs from the reactant by both a hydrogen ion and a water molecule (24a).

Examples of case 1 include the acid catalyzed hydrolysis of sucrose (25), β-propiolactone (26), β-butyrolactone (26), methylal (27) the decomposition of trioxane (28) the depolymerization of paraldehyde (29) rates of isotopic halide-ion exchanges and racemization of some secondary alkyl halides, (30), and hydration of isobutene (31).

Some clearcut examples of case 2, where the rate has been shown to be proportional to H_3O^+ concentration--but not H_0, include the hydrolysis of γ-butyrolactone (26), and the iodination of acetophenone (32).

The effect of added electrolyte on the acidity function has been evaluated qualitatively and quantitatively (9)(33) and extended to its effect on reaction rates (34). It has been observed that H_0 increases with the addition of LiCl, NaCl, NaBr, $NaClO_4$, KCl, and decreases with the addition of CH_3/SO_3Na, Me_4NBR, Et_4NBr. Because the base being acted upon is neutral, the effect cannot be held to be general for all weak bases.

A Related Acidity Function - J_0

The H_0 acidity function is only valid for neutral bases reacting in the following manner

$$B + H^+ \rightleftharpoons BH^+$$

However, secondary bases are also of interest, and a new acidity function must be derived to accommodate these bases. They react according to the reaction:

$$ROH + H^+ \rightarrow R^+ + H_2O \quad [4]$$

The J_0 acidity function is defined by means of the equation (35):

$$J_0 = -pK_{ROH} - \log \frac{C_{R^+}}{C_{ROH}} \quad [5]$$

K_{ROH} represents an equilibrium constant for reaction [4]. Several investigators have worked on J_0 values (36). J_0 may be related to H_0 by the relationship:

$$J_0 = H_0 + \log a_{H_2O} - \log \frac{f_{BH^+} f_{ROH}}{f_B f_{R^+}}$$

Gold and Hawes (37) suggest that the last term cancels out, giving an approximate $J_0 = H_0 + \log a_{H_2O}$. This approximation is only good for concentrated acid solutions $> 75\%$ H_2SO_4. Other symbols (H_R, C_0) have also been suggested for similar functions.

The usefulness of the J_0 function has been demonstrated by its parallel to the rate of nitration of nitrobenzene, and the rate of oxidation of formic acid by nitrous acid and H_2SO_4.

Excellent reviews on the subject are available (25,37).

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NUCLEAR QUADRUPOLE COUPLING

David K. Roe October 29, 1957

Introduction

Spectroscopy in recent years has grown to include absorption and emission phenomena over the entire available spectrum. Exploitation of the remaining spectral region, the microwave region, had its real beginning in 1946, though the first paper was published in 1934 by Cleeton and Williams[1]. The rapid development of radar, or more explicitely, short wavelength sources, during World War II is responsible in part for the sudden activity. Since then, the wavelength limits have retreated to the extent that the shortest wavelengths have over lapped the longest wavelengths measured with infrared equipment. The general wavelength region extends from about 1 mm to 30 cm (300,000 Mc/sec. to 1000 Mc/sec.).

A more workable definition of the boundaries of the microwave spectrum would be that region in which rotational energy transitions of molecules are observed. Only molecules having a permanent dipole are capable of absorbing electromagnetic radiation by rotational energy transitions. Superimposed on the rotational spectra are the nuclear effects. This hyperfine structure can be resolved with microwave equipment and yields information on the chemical bond(s) in the molecule. The goal of the chemist is to know the electronic distribution throughout the molecule. Nuclear quadrupole coupling is able to reveal the electronic distribution as seen from one point in the molecule.

The molecular and nuclear requirements for quadrupole coupling definitely impose limits on the application of this method. The nucleus must have a spin of greater than 1/2, in units of $h/2\pi$, for it is the coupling of the spin, I, with the molecular rotational vector, J, which produces the hyperfine structure in the spectrum. Nuclei which have spins of greater than 1/2 have an ellipsoidal charge distribution. A quantity Q is defined as the quadrupole moment and is a measure of the deviation of the nucleus from spherical symmetry. With respect to the axis of spin, Q is positive for prolate and negative for oblate ellipsoids. In an inhomogeneous electric field the various orientations of a quadrupole have different energies. In molecules, inhomogeneous electric fields are present when the electrons and other charges about a nucleus have a nonspherical charge distribution. The potential energy of a quadrupole nucleus is a function of its orientation, which is quantized, and these different energy states are responsible for the hyperfine structure of rotational lines.

Nuclear Quadrupole Coupling Constants

The energy of the quadrupole coupling is a function of eQq^2 and known functions of the quantum numbers I, J and K. The latter is the quantum number associated with the component of angular momentum along the symmetry axis. The product eQq is called the

nuclear quadrupole coupling constant and is composed of the charge on the proton e, the nuclear quadrupole moment Q and the field gradient q, which is d^2V/dz^2 along the fixed axis z. The potential energy notation is V. Measurement of eQq and knowing the value of Q for the nucleus permits the calculation of q which is a function of the environment of the quadrupole nucleus and therefore is connected with the bonding of that atom. There are two major sources of nuclear quadrupole coupling constants[3,4]. If the sample can be studied in the gas phase at low to moderate pressures, microwave absorption is used. In the case of solids, pure quadrupole resonance studies can be made in the radiofrequency region. Atomic and molecular beam methods have also been used to obtain coupling constants. Quadrupole moments have been measured by optical and microwave spectroscopy, atomic and molecular beam techniques and nuclear resonance absorption. Since Q is the same for a given nucleus it can be obtained from coupling constants in the simpler cases where q is calculable from theory. In the case of atoms, as Cl, Br and I, q is calculable from experimental data as nuclear magnetic hyperfine structure or fine-structure splitting of atomic spectra. Very accurate values of eQq (atomic) are known for Cl^{35}, Br^{79} and I^{127}. Tables of both eQq and Q are given references 3 and 4.

Interpretation of Coupling Constants

Knowning the field gradient q at a particular nucleus is only a step toward the elucidation of the chemical bond. The various factors which contribute to the field gradient must be considered in the light of their relative importances[5,6]. By far the most significant contributions to the field gradient are made by those valence and lone pair electrons which have a high probability of being near the nucleus. Small contributions are made by the other charges present in a molecule but since the effect varies inversely with the cube of the distance, the effect is small and may often be neglected. Although polarization of the inner shells may appear to greatly affect the field gradient, it is usually very small. In iodine, for instance, polarization amounts to about 2% of the total contributed by a single valence p electron[7].

Returning to the effect of lone pair and valence electrons the contributions may be considered under the topics of overlap, ionic character and hybridization. Overlap of atomic orbitals is probably insignificant[8] compared to valence electrons. Its effect has been calculated by the use of overlap integrals[9,10].

The two remaining factors are generally depicted as the major contributors to the quadrupole effect. The change in quadrupole coupling with ionic character can best be described in a specific example. Thallous chloride serves this purpose adequately[11]. Consider first that the bond is covalent. The thallous nucleus experiences, on the average, a potential field due to one electron since the remaining shells are filled and hence are spherically symmetrical. This extra 6p electron produces a field gradient

q_{mol} equal to q_p^{tl}, which is same as in a single thallous atom. The chlorine atom is surrounded by filled shells except one, which has a defect of a 3p electron. The field gradient is noted $q_{mol} = -q_p^{cl}$.

If the bond is purely ionic, each nucleus has only filled electron shells surrounding it so the value of q_{mol} is zero for each. Between the two extremes, which is the actual case, there is a contribution from each type of bond. This is given by the product of q for the s structure concerned and its fractional importance. Therefore for thallium

$$q_{mol} = (1-x)q_p^{tl} + xq^{tl^+}$$

when the bond is ionic by a fraction x. The last term is zero, as discussed above.

Similarly for chlorine,

$$q_{mol} = -(1-x)q_p^{cl}.$$

In terms of the experimentally measured quantities $eQq_{mol}^{tl^+}$ and $eQq_{mol}^{cl^-}$ the above equations become

$$eQq_{mol}^{tl} = (1-x)eQq_p^{tl}$$

$$eQq_{mol}^{cl} = (1-x)eQq_p^{cl}$$

The term (1-x) is known as U_p, the amount of unbalanced p electrons oriented along the bond axis. With proper regard to the sign convention in use,

$$U_p = -eQq_{mol}^{tl}/eQq_p^{tl}$$

$$U_p = eQq_{mol}^{cl}/eQq_p^{cl}$$

A few representative values are listed for chlorine and bromine compounds.

	eQq (Mc/sec.)	U_p
Cl^{35} (atomic)	-109.74($-eQq_p$)	
KCl	0.041	0.01
TlCl	-15.8	0.14
BrCl	-103.6	0.94
Br^{79} (atomic)	769.8($-eQq_p$)	
KBr	10.24	0.013
BrCl	876.8	1.14

Low values of eQq indicate high ionic character. The actual values of U_p should not be taken as a true indication of fractional ionic character because there is one more factor to be considered: hybridization.

Covalently bonded chlorine should show a coupling constant of very nearly the same magnitude as in atomic chlorine. The fact that most covalent chlorine atoms show an eQq of about 80 Mc/sec. indicates that the bond is not a pure p bond. It is generally assumed that hybridization[12] occurs in such cases and lowers the

measured value of eQq. Unfortunately this results in an equation of two unknowns and one measured quantity. The quadrupole effect cannot distinguish between the amount of hybridization and ionic character.

It becomes necessary either to stop at this point and be satisfied with a composite coupling constant or to attempt to evaluate one of the two unknowns separately. (Of course the latter is the only view taken by the leading workers in the field.) Attempts have been made to correlate ionic character and electronegativity differences. The resulting curves by Gardy[6,10,13] and Dailey and Townes[14] were constructed semi-empirically from coupling data of halogen compounds. The purpose of these curves is to give a value for the ionic character of a particular bond, knowing the electronegativity difference of the atoms concerned, so that the hybridization can be calculated from the quadrupole coupling constant.

The curves of Gardy and Dailey and Townes differ in the region of small ionic character. The difference is primarily due to the belief by Gardy[15] et al that hybridization does not exist in the regions of pure covalent or pure ionic bonding while Dailey[16] and Townes interpret the experimental evidence as indicating that a covalent chlorine bond is an sp-hybridized atomic orbital. Both views are open to a certain amount of criticism.

In several instances quadrupole coupling constants have provided direct proof of the valency of atoms in molecules. A notable example is nitrogen in NNO[17] and CH_3NC[18,19,20]. Nitrogen has a quadrupole coupling constant of about -4 Mc/sec. when triply bonded. Measurements of the coupling of the nucleus of $N^{14'}$ in $N^{14}N^{14'}O$ show that it is quadruply bonded since $eQq = -0.08$ Mc/sec. Similiarly in $CH_3N^{14}C$ the nitrogen is quadruply bonded for its $eQq < +0.5$.

Conclusion

In spite of its inability to differentiate between field gradients caused by ionic character and sp-hybridization, nuclear quadrupole coupling constants do indicate some important aspects of electronic distribution near the quadrupole nucleus. In some cases very specific and unique information is obtainable. Continuing investigations of chemical bonds will undoubtedly rely on nuclear quadrupole coupling for much information.

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Electronegativity and Atomic Number Relationships

John A. McLean November 12, 1957

Introduction

Early discussions of molecules such as the hydrogen halides treated them as consisting of ions which deformed each other to some extent. When ions approach each other closely, the attraction of the cation for the electron atmosphere of the anion and the simultaneous repulsion of the nucleus of the anion result in deformation or polarization of the anion. Ion deformation is favored by a number of factors (1) thereby making it difficult to describe the nature of the chemical bond between two atoms in terms of mutual polarization and deformation of ions. Pauling (2) defines electronegativity as the power of an atom in a molecule to attract electrons to itself. If there is a large difference in the electronegativity of two atoms formation of bonds which are predominately ionic will result. As this difference becomes less pronounced, bonds become increasingly covalent in character. Electronegativity can be used to describe the relative electron distribution in a heteronuclear molecule and to describe each covalent bond in terms of its partial ionic character. If B is more electronegative than A in molecule AB, then the ion pair A^+B^- would be expected to contribute more to the ionic character of a covalent bond between A and B than the ion pair A^+B^-. However, the determination of a precise electron-distribution map of a molecule presents a difficult problem because such information cannot be gained directly from experiment.

Several methods of measuring electronegativity in a qualitative manner have been proposed. The first of these was derived by Pauling (3) who postulated the additivity of the energies of normal covalent bonds. Data was collected on the heats of formation and heats of combustion of gaseous molecules and used to evaluate the energies of various bonds (2). It was found (3) that deviation from additivity, , is positive for all bonds and increases as the amount of ionic character of the bond increases. This procedure could be used to determine the amount of ionic character in bonds and permitted the localization of the atoms involved on an electronegativity map. This information has proven to be invaluable to the chemist in explaining as well as predicting the properties of compounds.

Pauling's Electronegativity Scale (2)

Additivity of normal covalent bonds suggests that a covalent bond between atoms A and B will be intermediate between the values of bonds A-A and B-B. The difference between the actual bond strength and the arithmetic mean bond strengths of the corresponding symmetrical bond strengths can be represented as

$$\Delta = D(A-B)-1/2\ \ D(A-A)+D(B-B)\ .$$

If the additivity postulate were true actual bond energies between unlike atoms would always be equal to or greater than the arithmetic mean of the corresponding symmetrical bond energies. Pauling found that this postulate of additivity is valid for a large number of single bonds but exceptions to this rule were realized at the beginning. The alkali metals form diatomic molecules, which are

present in small concentrations in their vapors. They also form hydrides. Calculation of the ionic resonance energy of these compounds from the additivity postulate yielded negative values. A quantum-mechanical treatment of the one electron bond led to the conclusion that the postulate of additivity should be replaced by a similar postulate involving the geometric mean of the bond energies(4). This leads to a new expression for ionic resonance energy defined as

$$\Delta' = D(A-B) - D(A-A)D(B-B)^{1/2}.$$

' should always be greater than or equal to 0. In many cases the bond energies do not differ greatly and in such cases the ionic resonance energy may be calculated by either postulate. Pauling's electronegativity scale of the elements (2) was calculated from single bond energies. The calculated values of do not satisfy a linear relation among the elements. However, the square roots of values do satisfy a relation of this sort. The square roots of values may be taken as electronegativity differences between bound atoms. Electronegativity differences ($x_a - x_b$) may be converted to electron volts by the expression (2):

$$x_a - x_b = 0.2084\ \Delta^{-}$$

To assign electronegativities to the elements themselves, it is necessary to fix arbitrarily some point on the scale. The most electron gative element, fluorine, is consequently given the value 4.0 in order to make all other values positive. Values are assigned to other elements on the basis of experimental values. Pauling adjusts this scale so that a linear relationship exists among the greatest majority of elements. This was done with an additive constant so chosen as to give carbon a value of 2.5 relative to the value of 4.0 for fluorine.

Criticisms of Pauling's Scale

Pauling has allotted values to thirty-three elements (2). Of this total only fourteen could be obtained directly. For the majority of the elements, values of single-bond energies are unknown. In order to extend this thermochemical treatment estimates had to be made for many unknown single bond values.

A single electronegativity value should not be expected to be constant in all possible compounds involving such an element (5). Hybridization as well as the immediate environment of an atom should affect its power to attract electrons to itself. Pauling also assumes that dipole moments can be used to calculate the degree of ionic character in a molecule (2). Modern studies indicate that dipole moments depend on a number of factors such as lone pair electrons, hybridization, etc. (6). The contribution of ionic character to the total dipole moment of a molecule may or may not be apparent from measurements.

Refinements of Pauling's Scale

Mulliken's Electronegativity Scale

Mulliken (5) has suggested that the average of the ionization potential and the electron affinity of an atom should be a suitable measure of the electronegativity. This definition may be expressed by the relationship:

$$x_a = 1/2(I_a + E_a)$$

However, I_a is not (in general) a physically observable ionization potential of A but is the "valence-state" ionization potential; similarly E_a is the "valence-state" electron affinity. The meaning of valence state used in this connection may be clarified by examining the hydrogen chloride molecule. The ground state is the singlet state. The hybrid structure of the molecule may be represented as

$$\Psi_{HCl} = \epsilon_1 \Psi_{(H-Cl)} + \epsilon_2 \Psi_{(H^+Cl^-)} + \epsilon_3 \Psi_{(H^-Cl^+)}.$$

The ground state for Cl^- is ^1S, and this on combination with H^+ can give a singlet state. But the ground state of Cl^+ is ^3P, which can give only triplet states on combining with H^-, ^1S. The two low-lying excited states, ^1D and ^1S of Cl^+ will give a singlet on combination with H^- and both will contribute to the valence state of Cl^+. The ionization process to produce Cl^+ will be a suitably weighted mean of the two processes

$$Cl(^2P) - e^- \rightarrow Cl^+(^1D) \text{ and } Cl(^2P) - e^- \rightarrow Cl^+(^1S).$$

This approach (5) attempts to take hybridization effects into account. The fact that acetylene is more acid than methane can be explained in terms of increased electronegativity as carbon goes from sp to sp^3 hybridization. This scale has a somewhat better theoretical basis than that of Pauling's. The valence state ionization potentials were calculated from spectroscopic data. Moffit (7) devised a rather rigorous vector procedure for calculating these data with considerable accuracy.

Gordy's Electronegativity Scale

Gordy (8) found an empirical relation of the form

$$k = aN(x_a x_b/d_{ab}^2)^{3/4} + b$$

which applied to the bonds of a large number of diatomic and simple polyatomic molecules. In this equation x_a and x_b are the electronegativities of the atoms forming a given bond AB; n, k and d_{ab} are the bond order, bond-stretching force constant, and bond length respectively. a and b are constants for certain broad classes of molecules. By means of this relation the electronegativity scale was extended (8) to include a total of fifty-two elements. Gordy also made an attempt to define the electronegativity of an element in the absolute sense rather than in terms of some other element (9).

Sanderson's Stability Ratios

Sanderson (10, 11, 12) has proposed that covalent radii can be used to set up an electronegativity scale. For purposes of comparing the relative compactness of electronic shells of atoms of different atomic number a "stability ratio" (SR) has been devised. This is the ratio of the electron density of an atom or ion to the electron density of an isoelectric inert atom, real, or hypothetical and determined by interpolation between real values. The concept of maximum stability at unit stability ratio (12) helps to explain the increase in stability when electrons are attached. The acquisition of a partial negative charge results in expansion of the electronic sphere which is considered to bring about a better balance of forces within the atom and also reduces electronegativity. One of the major

differences between Sanderson's scale and those of Pauling and Mulliken is the alternations as one passes from the lighter to the heavier elements in a given group in the periodic table.

Applications

Kinetics

Studies have been made of electrolytic dissociation and degree of hydrolysis of ionic reactions of dimethyl germanium dichloride (13). When these data were compared with data obtained from corresponding reactions of dimethyltin dichloride insight was gained as to the relative electronegativities of these two compounds. This study indicates that the electronegativity value of germanium is not in line with the other members of this family.

Spectroscopy

Measurement of the nuclear quadrapole coupling constant can indicate the electronic nature of the chemical bond (14). The coupling constant for free chlorine is -110 Mc./sec. Coupling constants (15) for chlorine in some of its compounds are shown in Table I.

Table I

compound	coupling constant for Cl
Cl_2	- 108.5 Mc./sec.
CH_3Cl	- 83.0 "
NaCl	0

The electronic environment of the chlorine nucleus in sodium chloride is nearly spherical. If chlorine forms a pure p-bond, the coupling constant should be the same as for free chlorine, and thus the above data indicate that Cl_2 evidences almost a pure covalent bond. The methyl chloride constant is difficult to interpret because partial charge transfer or more s character could be responsible for the reduction in the coupling constant. Gordy (14) has shown that the coupling constant decreases as the electronegativity difference between the atoms in a molecule increases. Since the number of unbalanced p electrons (Up) can be experimentally determined, the following linear relationship has been found to be useful

$$(1-Up) = \frac{x_a - x_b}{2}$$

Nuclear Magnetic Resonance studies (16) have shown that there is a relation between the chemical shifts of hydrogen atoms in methyl halides and the electronegativity of the halogen. Electronegativity values may be obtained in this manner if a series of compounds are selected whose hybridization of orbitals in the appropriate bond is approximately constant.

Bond Lengths

Schoemaker and Stevenson (17) showed that single bonds between atoms of different electronegativity tend to be shorter than the sum of their covalent radii even when double bond resonance is not present. This effect is most noticeable with bonds to F or O, which have a high electronegativity as compared with other atoms. The approximate

empirical rule,

$$R = r_a + r_b - \beta|x_a - x_b|$$

can be used for calculation of the interatomic distance R from the covalent radii v_a and v_b of the bonded atoms A and B, when x_a and x_b are the electronegativities of the atoms and $\beta = 0.09$. Gordy (18) has found that a value of 0.06 for β gives closer agreement with observed values. This same constant works for double bonds but substitution of 0.03 for β is needed to correct for triple bonds.

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The Chemistry of the Silyl Group

Charles T. Lynch

November 19, 1957

Introduction

The $-SiH_3$ group is known as the silyl group. Compounds containing this group are formal analogues of the methyl compounds. An excellent review on silyl compounds has recently appeared.[1] Although silyl and methyl compounds often have the same type formula, there are important differences in properties. There are five basic criteria of comparison:[2] both have normal covalence of four, normal bonding is tetrahedral in both, silicon is larger and heavier, silicon is less electronegative, and silicon may have a coordination number greater than four by utilizing its empty 3d orbitals.

The decreasing electronegativity results in a reversal in polarity of the Si-H bond compared with the C-H bond. The Si-H bond is more similar to the C-Br link.[1] The larger Si atom is sterically more vulnerable to attack and the ability of silicon to increase its coordination number to 5 or 6 greatly eases the formation of reaction intermediates.[1] The Si-H bond energy is less than the C-H bond energy; most other bonds formed, such as with oxygen, are stronger. Thus it is not surprising that most silyl compounds are more reactive and exhibit different properties.

Examination of the melting points of analogous pairs of methyl and silyl compounds is not too instructive, probably due to crystal structure differences arising from a larger silicon atom.[1]

Plotting of boiling points of the analogues against each other leads to linear results. The molar heats of vaporization should then be similarly linearly related since the Trouton constants are similar. The silyl compounds boil at higher temperatures except for the halogen derivatives. This might be due to lower intermolecular attraction because of their lower dipole moments.[1]

Pi-Bonding in Silyl Compounds

There is very good physical and chemical evidence for pi-bonding in silyl compounds. Other explanations for observed bond lengths and angles, dipole moments, stability of addition compounds, etc., cannot satisfactorily explain the evidence.[1,3,4]

The shortening of silicon-halogen bond lengths was first ascribed to a resonance between simple polar Si-X and doubly bonded Si=X.[5] Use of covalent bond radii corrected for ionic character, however, does not shorten the calculated bond lengths nearly enough.[6,3] It has been argued that a second row element is too large for sufficient overlap of d(pi)-p(pi) orbitals for any double bond character, and that a closer approach between atoms than the additive covalent radii is possible before inner-shell repulsions establish the bond distance.[7] Sufficient overlap, however, has been demonstrated where a sigma bond already exists between the atoms involved.[8]

The dipole moment of silyl chloride is much smaller than expected, being much smaller than that of the carbon and germanium analogues.[9] Microwave spectra show the same result for bond lengths and Cl quadrupole coupling.[10] The assignment of 20% ionic; 40% ionic and 30% double bond; and 45% ionic, 15% double bond character to C-Cl, Si-Cl, and Ge-Cl respectively fits the experimental values well.[10] Similar results were obtained with silyl bromide.[11]

Nuclear magnetic resonance measurements show that the hydroxylic hydrogen of an organo-silanol is more protonic than that of its carbon analogue.[12]

Electron diffraction studies indicate that trisilyl amine is planar, which we would expect if the N-Si bonds have partial double-bond character. Trimethyl amine is pyramidal.[13] Infra-red studies support a linear silyl isothiocyanate structure; the carbon analogue is non-linear.[14]

A number of compounds have been characterized that have coordination numbers greater than four, including $SiF_4(en)$, $SiF_4(en)_2$,[15] $SiF_4(py)_2$, $SiF_4 \cdot 2NH_3$, and $SiF_4(DMF)_2$.[16] The last two cases seem to indicate the same octahedral stretch of Si-F as in Na_2SiF_6, by infra-red spectroscopy.[16]

The more electronegative the element, the stronger the pi-bond to silicon. In a substance like trisilyl amine the donor power of the nitrogen atom is virtually lost due to the back coordination to the empty silicon d orbitals.[8,17] The order of stability of addition compounds in the following series towards boron trimethyl is illustrative:

$$N(Me)_3 > NMe_2SiH_3 > NMe(SiH_3)_2 > N(SiH_3)_3$$

Addition compounds for the last two do not form. With boron trichloride and trifluoride, weak addition compounds are formed with the trisilyl amine and strong ones with the trimethyl amine.[17,18]

A connection has been found between the Si-H bond parachor in a compound and the pi-bonding of the silyl compound.[19]

The use of the pi-bonding concept enables us to explain a great deal of the chemistry of the silyl group.

The Silicon Hydrides

The series of hydrides Si_nH_{2n+2} is known from silane, SiH_4, through the hexa-silane, Si_6H_{14}. Germanium hydrides are known only through Ge_3H_8 and tin only as SnH_4. The saturated silicon hydrides are colorless gases or liquids, and very highly reactive. They were originally prepared at low temperatures by the action of dilute HCl on Mg_2Si. Separation is accomplished by fractional distillation.[20] Their properties have been studied only to a limited degree[21] because they are hard to handle because of their reactivity.[22] Silane is more easily prepared by the reaction of Mg_2Si with NH_4Br in liquid NH_3. More recently the use of $LiAlH_4$ has been reported, for directly reducing the halo-compounds of Si, Ge, and Sn. Good yields of SiH_4 have been obtained.[23] The higher hydrides are very unstable even at low temperatures, yielding the lower hydrides and solid unsaturated hydrides $(SiH_2)_x$. At higher temperatures (500°) these, and the

lower hydrides decompose completely to Si and H_2. There is some disagreement concerning the mechanism involved. For di- and tri-silane, the formation of free radicals is indicated by the polymerization effect the decomposition has on ethylene.[24] For mono-silane an alternate mechanism has been proposed:[25]

$$SiH_4 \rightarrow SiH_2 + H_2 \quad ; \quad SiH_2 \rightarrow Si + H_2$$

The hydrides are strong reducing agents. They react vigorously with the free halogens, are spontaneously inflammable and explosive in air, hydrolyze rapidly in the presence of aqueous alkali, and are stable in pure, or slightly acidic water.[20] All the hydrides except silane react readily with $CHCl_3$ in the presence of $AlCl_3$.

Silyl Compounds of the Halogens and Pseudo-Halogens

The silyl halides are prepared from the hydrogen halide and silane, using an aluminum halide catalyst.[20,26] More convenient preparative methods entail reduction of $SiCl_4$ with HCHO at elevated temperature over an alumina catalyst for silyl chloride (SiH_3Cl), the reaction of silane with solid bromine at low temperatures to obtain the bromide, and interaction of silyl chloride with antimony trifluoride for making the fluoride.[1]

The reactions of silyl iodide with AgNC and AgNCS have been used to prepare SiH_3NC and SiH_3NCS.[27] Only the tetra-cyanate is formed using AgNCO. The derivatives appear to be iso forms; their infra-red spectra have been studied.[28] They hydrolyze too rapidly to use this means of determining structure, as is done with the methyl compounds[27].

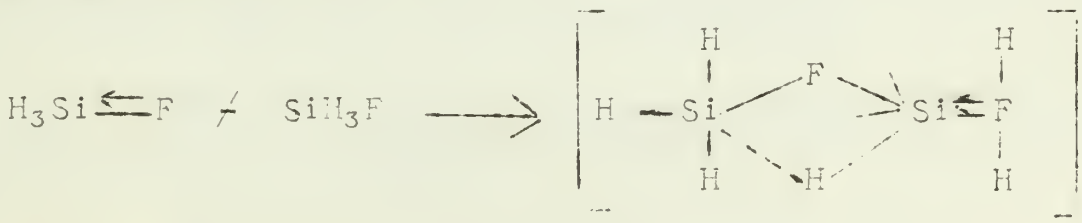
Treatment of disilane with the hydrogen halide in the presence of the aluminum halide yields disilanyl chloride and bromide. Higher substitution products are formed but have not been separated.[20]

The halides are hydrolyzed instantaneously by water to disiloxane and the hydro-acid. In aqueous alkali, hydrogen is liberated.[1]

All the halides tend to disproportionate:[26,29]

$$2SiH_3X \rightarrow SiH_2X_2 + SiH_4$$

The tendency is greatest for the fluoride, almost negligible for the iodide. We can explain this by assuming that the pi-bond can act in an intermolecular fashion in the formation of an activated complex.

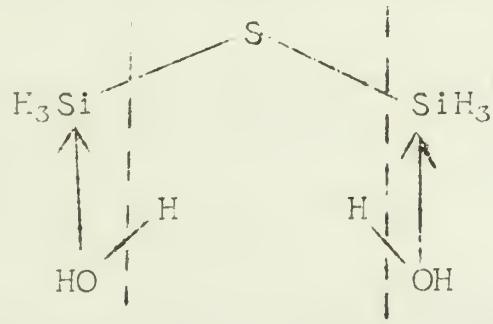


The greater disproportionation rate for the disilanyl halides can be explained by the decreased charge on the silicon not attached to the chlorine, making it more vulnerable to intermolecular bonding.[1] The rate would be fastest for the halide that forms the strongest intermolecular pi-bond, this being the most electronegative in the series.

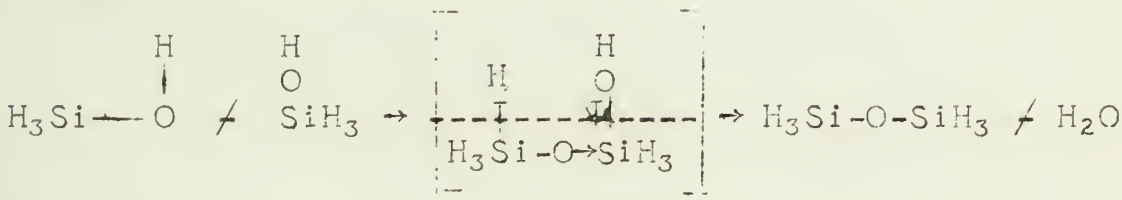
Silyl Compounds of Group VI Elements

Disilyl ether is formed as the hydrolysis product of many silyl compounds, such as the halides. Silyl alcohol is believed to have transitory existence as an intermediate in the hydrolysis of both silyl chloride and bromide.[1]

Disilyl sulfide and selenide are formed by the action of silyl iodide on HgS and Ag_2Se.[30] Both hydrolyze rapidly to silyl ether and the respective acids. A gelatinous intermediate is formed which rapidly decomposes into the hydrolysis products.[30] An intermediate with coordinated water has been proposed.[1]



The H_2S splits off, followed by rapid condensation of the silyl alcohol.



Disilyl ether, sulfide, and selenide all react with the halogens, the ether explosively to form $SiCl_4$ and $(SiCl_3)_2O$. With solid iodine, silyl iodide and the free S, Se, or O_2 are liberated. No onium compounds are formed with methyl iodide and no sulfonium compound from disilyl sulfide and silyl iodide.[30] The sulfide does not form an addition compound with mercuric chloride or iodide. These are indications of a loss in coordinating power by the central atoms, due to their back coordination to the silicon.[1]

The silyl mercaptan is formed in an equilibrium reaction between disilyl sulfide and hydrogen sulfide at room temperature.[30] The condensation reaction of SiH_3SH to form $(SiH_3)_2S$ is slower than the silanol condensation. This is to be expected if intermolecular pi-bonds form on the basis of the electronegativity.

A higher ether $(SiH_3SiH_2)_2O$ has been synthesized by the hydrolysis of either disilanyl chloride or bromide. All the above compounds are colorless liquids or gases.[1]

Silyl Compounds of Group V Elements

The mono- and disilyl amines are formed from silyl chloride and excess NH_3; an excess of silyl chloride yields trisilylamine, $(SiH_3)_3N$.[1] N-substituted silylamines are obtained from substituted amines:[17,31]

$$SiH_3Br + NHMe_2 \rightarrow SiH_3NMe_2 + HBr$$

Quaternary compounds result from this type reaction using NMe_3.[31,32] Addition compounds of silyl chloride through $SiCl_4$ with NMe_3 have been reported.[33] The quaternary and addition compounds are colorless solids, whereas the other amines are colorless liquids and gases.[1] The mono and disilylamines condense rapidly to form trisylamine and NH_3, possibly by intermolecular pi-bonding followed by a splitting out of NH_3. The fact that the analogous phosphine and arsine derivatives condense slowly is expected from electronegativity values. Trisilyl amine is very unstable and reacts vigorously with water to give silica, NH_3, and H_2.[1]

The alkyl substituted amines are more stable. The disilyl methyl and ethyl amines and trisilylamine react with HCl to form silyl chloride.[31]

The addition compounds with boron derivatives have already been mentioned. The trisilylamine-boron trichloride and fluoride complexes lose the silyl halide and yield $(SiH_3)_3N{=}BX_2$. These condense to form a liquid trisilyl trihalo borazole $(SiH_3NBX_3)_3$, which has not yet been studied in any detail.[17,18,34]

Tetra silyl hydrazine has been prepared and studied in some detail. It forms no adducts with silyl iodide or trimethylamine.[4]

$(SiH_3NMe_3)Cl$ can be used as a silylating agent.[31] Heating phosphine and silane produces SiH_3PH_2. Interaction of white phosphorous with silyl iodide produces a mixture of iodosilylphosphines. Arsenic with silyl iodide yields a similar mixture; only di-iodosilyl arsine has been characterized. No alkylsilyl arsines or phosphines are known, but the quaternary phosphonium and arsonium compounds are known.[32]

The phosphonium compounds are formed from the silyl halides and the alkyl phosphines. Silyl iodide and trimethyl arsine yield unstable SiH_3AsMe_3I; arsine is obtained on hydrolysis. Silyl iodide and mercuric arsenide give the tetrasilyl arsonium iodide. K_3As reacts with silyl iodide to give the di- and trisilyl arsines.[1]

Silyl Compounds of Group IV Elements

The reaction of silyl chloride with an organo-metallic compound produces an alkyl or phenyl substituted silyl group:[20]

$$SiH_3Cl + ZnMe_2 \rightarrow SiH_3Me + ZnCl_2$$

Reduction of a trichloride with $LiAlH_4$ is more often used:[23]

$$SiCl_3Me \xrightarrow[LiAlH_4]{} SiH_3Me$$

The preparation of mono and dichloromethyl silane has been accomplished in similar fashion:[35]

$$CH_2ClSiCl_3 \xrightarrow[LiAlH_4]{} CH_2ClSiH_3$$

CCl_3SiH_3 was not prepared by this method. All the alkyl and phenyl silanes are colorless liquids or gases. They are very stable and hydrolyze only slowly in aqueous alkali.

The fact that silane undergoes a Wurtz type reaction with sodium to give disilane is sometimes thought to take place by a free radical mechanism.[26] Attempts to demonstrate the existence of free radicals have not been conclusive thus far.[1]

No reproducible work on Grignard-type compounds has yet been presented.[36]

Reaction Series

A conversion series for silyl compounds has been proposed.[37] An acid replacement series is also postulated.[1] Both are substantiated by thermodynamic calculations.

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Inorganic Aspects of the Ziegler Catalyst

R. D. Vest

November 26, 1957

Until recently the production of polyethylene on a commercial basis has been carried out in an expensive, high pressure apparatus; the reaction being catalyzed by carefully controlled trace quantities of oxygen. Several new catalyst systems have been discovered which convert many olefins, ethylene included, into high polymers with great efficiency. This seminar will deal mainly with the catalyst systems of Ziegler and Natta because of the availability of information in the journals. Most of the information on the equally important industrial processes is covered in patents.

As early as 1938, du Pont obtained a patent (1) in which it was claimed that ethylene can be converted into a polymer by a mixture of a lithium alkyl and a hydrogen contact catalyst such as nickel or nickel oxide on a silica support. Several years later Fisher (2) converted ethylene into lubricating oils using aluminum chloride and in one experiment he obtained a small amount of a white solid, presumably polyethylene, when titanium tetrachloride and small amounts of aluminum powder were added to the aluminum chloride.

During the last decade Ziegler found that the reaction between aluminum triethyl and ethylene produced aluminum alkyls containing larger alkyl groups according to scheme I.

$$\text{(I)}\quad M(C_2H_5) + CH_2{=}CH_2 \rightarrow C_2H_5{-}CH_2{-}CH_2{-}M \rightarrow C_2H_5\,(CH_2{-}CH_2)_nM$$

$$M = Al/3$$

However, high polymers were not produced because of a side reaction (II) which takes place at various stages of the addition (3).

$$\text{(II)}\quad {-}CH_2{-}CH_2{-}M + CH_2{=}CH_2 \rightarrow {-}CH_2{=}CH_2 + C_2H_5M$$

On one occasion the routine synthesis of an aluminum alkyl by reaction I was attempted but no higher alkyl was obtained. Instead, the reaction gave a quantitative yield of butylene; i.e., the aluminum alkyl, contaminated with some unknown substance, catalyzed the dimerization of ethylene. In the search for materials which catalyzed the displacement reaction (II) (nickel in this case; others found to have the same effect were cobalt and platinum) it was found that compounds (notably chlorides) of group IV, V, VI metals, thorium and uranium included, minimized the displacement reaction and gave high polymers in good yield. Titanium was found to be one of the most effective metals and it was later observed that other reducing agents besides metal alkyls were equally good. Diethyl aluminum chloride (3) was found to yield an active catalyst in conjunction with titanium tetrachloride, as did Grignard reagents, other metal alkyls (CdR_2, $LiAlR_4$) and metal hydrides (both simple hydrides and borohydrides)(4,5). In general, it was found that compounds of metals which are not easily reducible to the free metal by a metal alkyl make the best cocatalyst. This process was quickly expanded to a commercial scale and is called the "Mühlheim Normal Pressure Polyethylene Process".

Since most metal alkyls react violently with air or moisture, the reactions are carried out in an inert solvent and atmosphere. The polymerization reaction is fast and efficient; the resulting polymers frequently have steriochemical properties which enhance their crystallinity and hence their commercial value (6,7,8).

Several generalizations can be drawn from the experiments which have been devised in an attempt to explain what the catalyst is and how it works. First, no one knows, exactly, the answer to either question and second, the answer is probably not a simple one. Since most of the catalysts are pyrophoric materials, the complex problem of heterogeneous reactions is complicated further by analytical problems.

There are three processes which may be operative in the polymerization reaction: an ionic, a radical, or a ion-radical process. Natta (9) has described a "bound anionic" mechanism in which the ion pair is on the surface of the catalyst. The data supporting this mechanism are: 1) among the elements which yield metal alkyl compounds of high catalylic activity are those metals which generate more intense electric fields and have small atomic radii (Be, Al, Li); 2) solutions of catalytically active soluble complexes show electrical conductivity, with migration of groups richer in alkyls to the anode; 3) termination of the polymerization process appears to involve transfer of a hydride ion to the aluminum atom, and 4) substances known to inhibit free radical processes do not effect the reaction (8).

A free radical process similar to the above anionic process can be described in which instead of a heterolytic cleavage of the metal-carbon bond there is a homolytic cleavage followed by the addition of a monomer unit. In these two processes, the polymerization takes place at a single reactive site, in much the same way as a plant grows from its roots.

The ion-radical process is different in that the radical is not localized at any particular point but moves over the surface of the catalyst, never being far removed from that surface.

With some idea of how a heterogeneous polymerization reaction may occur, the next question is what the actual catalyst is and what is its mode of action. Within the scope of an anionic process, the possibility of adding a mononomer unit to a titanium-alkyl bond or to an aluminum-alkyl bond exists. It is known that a mixture of titanium tetrachloride and a zinc or sodium alkyl has considerable catalylic activity but no claim is made as to whether a titanium alkyl is formed or not. Chemists at Metal Hydrides Inc. (11) have found that $NaH-TiCl_4$ systems are excellent catalysts as well as $NaH-AlCl_3-TiCl_4$ systems. Other catalytic systems which do not contain aluminum are $TiCl_4$ + Grignard reagents and $TiCl_4 + Sn(C_4H_9)_4$ (5). These data indicate that an aluminum-carbon bond is not necessarily involved directly in the catalysts action. On the other hand, Natta has conducted some experiments which indicate clearly that the alkyl group which starts on the aluminum compound ends up on the polymer chain. His data are summarized in the following table.

Table I

Ti Compound	Al Compound	Observation on Polymer
$Ti(C_5H_5)_2Cl_2$	$Al(C_2H_5)_3$	Produces polymer
$Ti(C_5H_5)_2Cl_2$	$(C_2H_5)_2O$ $Al(C_6H_5)_3$	Presence of phenyl groups
$Ti(C_5H_5)_2(C_6H_5)_2$	---	No polymer
$Ti(C_5H_5)_2(C_6H_5)_2$	$Al(C_2H_5)_3$	No phenyl groups
$TiCl_4$	$(C_2H_5)_2O$ $Al(C_6H_5)_3$	Presence of phenyl groups
----	$(C_2H_5)_2O$ $Al(C_6H_5)_3$	No polymer
$Ti(C_5H_5)(C_6H_5)_2$	$(C_2H_5)_2O$ $Al(C_6H_5)_3$	Presence of phenyl groups

All of the catalyst systems in Table I are homogeneous under the conditions of the experiments (benzene as solvent, 75-250°C.). These data can be interpreted to mean that the aluminum-alkyl bond is directly involved in the polymerization reaction since it appears that if phenyl groups are on the aluminum alkyl, these groups are incorporated in the polymer while the same is not true for titanium alkyls. Obviously, a simple hypothesis involving only one metal cannot explain all of these facts.

A further aspect of the catalyst composition is the oxidation state of the transition metal after it has interacted with the reducing agent. This question is complicated by alkylation of the titanium. According to Friedlander (13) when the catalyst system is $Al(C_2H_5)_3$ and $TiCl_4$, the titanium is completely reduced to the tripositive state with small surface quantities reduced to the divalent state. The second reduction is hindered by the fact that it is a heterogeneous reaction; Standard Oil Company workers believe this to be minor. On the other hand, du Pont chemists (4,5) believe divalent titanium to be the active species, at least in some cases. The reaction seems to be relatively insensitive to the exact nature of the titanium added since $TiCl_2$, $TiCl_3$, $TiCl_4$, $Ti(OH)_4$ may be used but the activity of the catalyst decreases as one goes through the series; the first two being about equal(6). It should be mentioned that du Pont workers have used lithium aluminum alkyls (notably hexyl and decyl) in conjunction with titanium, zirconium, or vanadium tetrachloride with considerable success(5).

Kinetic data, obtained by Natta (14) using crystalline $TiCl_3$ and $Al(C_2H_5)_3$, indicate the following: 1) There is an induction period which is independent of catalyst concentration or ratios and has been explained on the basis of the $TiCl_3$ crystals cleaving to produce active centers. If the reaction is stopped by terminating the monomer source and started again, there is no induction period. 2) The final rate of polymerization is proportional to the amount of $TiCl_3$ and monomer present and independent of the aluminum triethyl:titanium tetrachloride

ratio or the aluminum triethyl:monomer ratio.

Natta (15) has isolated a catalytically active complex for which the analytical data and chemical behavior indicate the formula $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ and states that this material has less activity than a mixture of $TiCl_4$ and $Al(C_2H_5)_3$. More recently, Breslow (16) reported the isolation of a complex to which he gives the formula $(C_5H_5)TiCl \cdot 1/2(C_2H_5)_2AlCl \cdot 1/2(C_2H_5)AlCl_3$. This complex was found to be poor except when the ethylene contained trace quantities of oxygen which, according to the authors, oxidizes the titanium to the plus four state.

Materials which initiate the polymerization of olefins are not limited to mixtures of metal alkyls and transition metal halides. Standard Oil Company has developed a process (17) in which molybdenum or nickel oxide, reduced by hydrogen at 250°C. on a charcoal support is used. This catalyst has the advantage that it can be easily adapted to a continuous process by regenerating with hydrogen or by the addition of "promoters". These promoters are hydrides of sodium, calcium, or lithium and there is some evidence that these materials enter into the polymerization reaction themselves (18). Phillips Petroleum Company has also developed a catalyst similar to that of Standard Oil Company. This catalyst is prepared by drying a solution of chromium trioxide on a silica support.

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MULTIPLE BONDING IN PHOSPHOROUS COMPOUNDS

Charles C. L. Hwa December 3, 1957

The study of multiple bonding constitutes a part of a comprehensive systematic study of the chemistry of phosphorous and its compounds. Like carbon, phosphorous is covalently bound to its neighboring atoms in all of its compounds, except for some metallic phosphides. Probably the major difference between carbon and phosphorous is that the former element is quite closely restricted to the use of s- and p- orbitals, because of the relatively high energy of d- orbitals in the case of first row elements; whereas, phosphorous, being a second row element, can use d- orbitals in bonding. For both carbon and phosphorous the most common hybridization for σ- bonding is approximately the tetrahedral sp^3. However, in order to form π - bonds, carbon must go to lower hybrids: sp^2 and sp. Phosphorous, on the other hand, does not do this but can employ d- orbitals for π-bonding (1).

Coordination of Phosphorous in its Compounds

The known coordination numbers exhibited by phosphorous in molecules or molecule-ions are 1, 3, 4, 5 and 6. These exhibit the geometry of p, p^3, sp^3, sp^3d and sp^3d^2 hybridization, respectively. A very large number of triply and quadruply "connected" P compounds are known, but there are only a few compounds of higher coordination number in which d- orbitals are involved in the σ- bond base structure. The singly "connected" P atom appears in compounds that exist only at very high temperatures.

Bond Shortenings and Excess Bond Energies

Van Wazer (2) has collected a large number of experimentally observed interatomic distances in P compounds and compared them with σ - bond distances, which were corrected for ionic effects, as taken from tables of Schomaker and Stevenson (3) and of Huggins (4). Following Pauling (5) (6), the bond shortenings were attributed to π - bonding. From the relationship between bond shortenings and π - bond character, the number of π - bonding electrons per σ - bond were obtained. This in turn gave the total number of π - bonds per P atom.

In a somewhat similar fashion, the heats of formation of P compounds obtained from monatomic gaseous elements were compared with values calculated from Huggins tables (7) of bond energy contributions. From the difference in energy, the amount of σ - bonding and the average number of π - bonds per σ- bond were calculated.

There is good agreement between the amount of π - bonding estimated from internuclear distances and from enthalpy data. Justification for attributing the observed effects to π - bonding also comes from a recent quantum mechanical calculation (8).

From this information, Van Wazer (2) has made several generalities concerning the P compounds, which are stable under normal conditions:

1. In those compounds in which P shares electrons with three neighboring atoms, there are three σ - bonds, with little or no π character from the P atom.

2. In those compounds in which P shares electrons with four neighboring atoms, there are four σ - bonds, with an average of about one π - bond per P atom.

3. When electrons are shared with five or six neighboring atoms, there is less than one full σ - bond for each "connection" between P and a neighboring atom with apparently very little π - bonding.

These generalities are dependent to a considerable extent upon the specific atoms connected to the P, and it is possible that the observed differences between the triply and quadruply connected P atoms may be attributed primarily to the individual ligands.

Several interesting family relationships appear among the quadruply linked P compounds, such as the phosphates. The degree of π - bonding varies depending on the geometry of the structures. The more branching the molecule has, the more unbalance there will be in the distribution of π - character among the four P-O bonds. This may be one reason for the "Anti-branching Rule" (9) in phosphates.

Pauling has shown that the shortening in internuclear distances, which he attributes to π - bonding, is found in the silicates, sulfates and perchlorates to about the same amount as in the phosphates (6). Moreover, Stone and Seyferth (10) have produced evidence to show that π - bonding occurs quite universally in quadruply linked Si compounds. Presumably, such π - bonding is generally found for elements below the first row of the Periodic Table when these elements exhibit a base σ - bond structure approximating sp^3 hybridization.

Pauling (6) has given an elementary explanation for the existence of considerable π - bonding in the oxyacids. This π - bonding could explain the reduction of the positive charge on the P atom which would be expected from the electronegativity difference between P and the atoms connected to it. This explanation seems to hold for quadruply connected P compounds, but further explanation is needed to justify the lack of π - bonding in these compounds even though the neighboring atoms are highly electronegative.

Nuclear magnetic resonance measurements have been made on a large number of P compounds (11). Although the quantitative explanation of chemical shifts has not been developed for P, the observed data seem to fit the qualitative picture. Van Wazer has concluded that in the triply connected structures, the π - bonding is unnecessary because of the presence of the fourth "abortive" bond (12), which appears as the hybridization changes from nearly pure p^3 in the case of PH_3 to nearly sp^3 in the case of PF_3. Increasing the electronegativity of substituent elements leads to the abortive bond which belongs entirely to the P and hence balances out the charge shift to the more electronegative elements bonded to the P. In the case of P linked to more than four atoms, the lower energy d - orbitals are already used in the σ - bond structure so that they are not available for π - bonding.

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POLARIZABILITY, BASICITY, and NUCLEOPHILIC CHARACTER of SOME INORGANIC ANIONS

G. L. DeTommaso December 10, 1957

It has been observed that a type of reaction with greater rate than expected occurs when certain nucleophilic reagents react with typical electrophilic reagents (1). Such large, easily polarizable nucleophiles as I^-, $S_2O_3^=$, thiourea, and SCN^- in reaction with alkyl halides disobey the usual rule that the rate correlates with the basicity of the nucleophilic reagent (2), being more reactive than indicated by its basicity. Such behavior is exemplified by the fact that thiourea, which has negligible basic properties, is two hundred times more reactive than pyridine toward alkyl halides; further evidence cited is the equilibrium constant of the following reaction:

$$CH_3CH_2O^{\ominus} + CH_2(CO_2Et)_2 \rightleftharpoons CH_3CH_2OH + {}^{\ominus}CH(CO_2Et)_2 \qquad Keq = 22$$

Nucleophilic scales have been obtained without consideration of polarizability and basicity (3-6). The usual procedures employed consisted of measuring rates of nucleophilic displacements for a series of anions on a single substrate, or measuring rates or yields of competitive reactions between two anions.

Swain and Scott (7) have found a four parameter equation correlating relative rates of various nucleophiles with several organic substrates in water solution. The reaction can be represented by N + S + E → [transition state] → products in which N and E are nucleophilic and electrophilic reagent respectively, and S the substrate. The free energy relationship correlating these rates is

$$\log {}^{k}/_{k_0} = Sn + S'e$$

where k_0 is the reaction rate constant for H_2O; k is the reaction rate constant for N; S and S' are substrate constants measuring the discrimination of the substrate among different N and E reagents respectively; n is a quantitative measure of the nucleophilic reactivity of N; and e is a measure of the electrophilic reactivity of E. Three corollaries follow directly from this equation. Since the reactions investigated were carried out in water solution, all calculations were made using the two parameter relationship

$$\log {}^{k}/_{k_0} = Sn.$$

In reactions with various substrates the order of reactivity of the reagents was found to be constant; however the selectivity of the nucleophilic anions varied widely from one substrate to another. From the overall data, the following n values were obtained:

TABLE I

N	n	N	n
$H_2\overline{O}$	0.00(reference)	$S_2O_3^{=}$	6.36
$CH_3COO^{\ominus}$	2.72	$2,4,6(NO_2)_3C_6H_3O^{\ominus}$	1.9
Cl^-	3.04	$SO_4^{=}$	2.5
Br^-	3.89	C_5H_5N	3.6
N_3^-	4.00	HCO_3^- or $HPO_4^{=}$	3.8
OH^-	4.20	$(NH_2)_2CS$	4.1
ϕ-NH_2	4.49	HS^- or $SO_3^{=}$	5.1
SCN^-	4.77	$HPSO_3^{=}$	6.6
I^-	5.04		

Taking the list as a whole, there is no correlation between base strength and nucleophilic power, but if we consider those nucleophiles which involve attack at the same atom (ex - $HS^{\ominus}$, $SCN^{\ominus}$, and $S_2O_3^{=}$) there is a correlation. It appears also that atomic diameter affects the n values since the high nucleophilic reactivity of the feebly basic anions containing elements below the first row of the periodic chart is probably correlated with the high polarizability of the valence electrons of the elements.

Of the nucleophiles in table I, $OH^{\ominus}$ was found to give abnormal results. A reasonable explanation can be put forth in considering repulsions, transition state stabilizations, and positive charge gradient at the center of attack.

The major shortcoming of this method is that a new set of n values are required for displacements on atoms other than carbon (8). To offset this difficulty perhaps a relationship involving free energy of solvation can be applied.

Foss (9, 10) has stated that nucleophilic reactivity of thio anions, $SX^{\ominus}$, towards S^{+2} and S_2^{+2} centers was found to increase with increasing redox potentials for the systems

$$2SX^{\ominus} \rightleftharpoons (SX)_2 + 2e^-.$$

The redox potentials of various thio anions were evaluated, and the nucleophilic reactivity was measured by reactions of the type

$$RSSX' + SX^{\ominus} \rightarrow RSSX + SX'^{\ominus}.$$

The relationship between oxidizability and nucleophilic strength can be explained easily from an electronic point of view. The potential is a measure of electron affinity, while in the polar displacement reaction, the driving force is the nucleophilic reactivity. The smaller the electron affinity, the higher the polarizability of the valence electrons, and therefore the greater is the portion of each electron pair available for bond formation. Therefore in the displacement reaction, an increase in the number of electron shells of the atom induces an increase in reaction rate.

A new equation combining a nucleophilic scale and a basicity scale for a correlation of rates of nucleophilic displacements and equilibrium data has been found (11). The equation is

$$\log {}^{k}/_{k_0} = \alpha En + \beta H$$

where ${}^{k}/_{k_0}$ is a relative (to H_2O) rate or equilibrium constant; H is the relative basicity of the donor to protons (given by $H = pK_a + 1.74$); En is the nucleophilic constant; and α and β are substrate constants. This new nucleophilic scale is based on electrode potentials since a linear relationship was found between the electrode potentials for oxidative dimerizations ($2I^- \rightleftharpoons I_2 + 2e^-$) and the n values of Scott and Swain (7). The nucleophilic scale, defined by $E_n = E^0 + 2.60$, is given in Table II.

TABLE II

N	E^0	E_n	H
NO_3^-	--	.29	(.40)
$SO_4^=$	-2.01	.59	3.74
$ClCH_2COO^-$	--	.79	4.54
CH_3COO^-	--	.95	6.46
C_5H_5N	--	1.20	7.04
Cl^-	-1.3595	1.24	(-3.00)
$C_6H_5O^-$	--	1.46	11.74
Br^-	-1.087	1.51	(-6.00)
N_3^-	--	1.58	6.46
OH^-	-.95	1.65	17.48
NO_2^-	-.87	1.73	5.09
ϕ-NH_2	--	1.78	6.28
SCN^-	--	1.83	(1.00)
NH_3	-.76	1.84	11.22
$(CH_3O)_2POS^-$	-.56	2.04	(4.00)
$C_2H_5SO_2S^-$	-.54	2.06	(-5.00)
I^-	-.5355	2.06	(-9.00)
$(C_2H_5O)_2POS^-$	-.53	2.07	(4.00)
$CH_3C_6H_4SO_2S^-$	-.49	2.11	(-6.00)
$SC(NH_2)_2$	-.42	2.18	.80
$S_2O_3^=$	-.08	2.52	3.60
$SO_3^=$	-.03	2.57	9.00
CN^-	.19	2.79	10.88
$S^=$	.48	3.08	14.66

The equation and scale have been tested using data on rates of displacement reactions on C, H, O, and S, equilibrium constants of complex ions, solubility product equilibria, and I_2 and S displacements. It was found that in many instances where calculated data showed a skewness, the calculated data using this new equation agreed very well with the experimental values.

Edwards (12) has gone one step further using this equation in that he has related nucleophilic strength of donor atoms to their polarizabilities (R_∞) and basicities (H) as shown in Table III.

TABLE III

N	E_n(obs.)	H	R	P	E_n(calc)
F^-	-.27	4.9	2.6	-.150	-.23
H_2O	0.00	0.0	3.67	.00	.00
Cl^-	1.24	(-3.0)	9.0	.389	1.21
Br^-	1.51	(-6.0)	12.7	.539	1.57
OH^-	1.65	17.5	5.1	.143	1.60
I^-	2.06	(-9.0)	19.2	.718	2.02
$S^=$	3.08	14.7	15.0	.611	3.11

The nucleophilic constant is given by

$E_n = aP + bH$ where $P \equiv R_{N}/R_{H_2O}$ and R is the molar refraction. Another form of the equation is

$$\log k/k_0 = AP + BH$$

which is a double scale equation for the correlation of rates and equilibria. Using these relationships of the new equation, it has been concluded that polarizability of more than one atom of a large nucleophile is involved.

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BASE STRENGTHS OF AMINES IN NON-PROTOLYTIC SOLVENTS

G. G. Giffin December 17, 1957

I. Introduction

Amine compounds give an alkaline reaction in aqueous solution and form salts with acids. The alkaline reaction is a result of the following process:

$$RNH_2 + HOH \rightleftharpoons RNH_3^+ + OH^-.$$

Basic strength is compared by use of pK_b values, where $pK_b = -\log \frac{[RNH_3^+][OH^-]}{[RNH_2]}$. These values have been determined for many amines in water and other protolytic solvents. Typical aliphatic amines are generally more strongly basic than ammonia while aromatic amines, for example aniline, are even weaker bases than ammonia.

Non-protolytic solvents include media where little or no proton exchange between solvent and solute can take place. These solvents are differentiating in character, that is, the intrinsic basicity of the solute is revealed in such media. To arrive at a measure of the affinity of a base for protons in these solvents, an acid must be added to the system. The determination of the position of equilibrium for $RNH_2 + HA \rightleftharpoons RNH_3^+ + A^-$, therefore, gives a quantitative evaluation of base strength.

II. Experimental Methods

A. Infra red measurements have been utilized to study the ion pair products of acid and base reactions in non-protolytic solvents. The use of this tool makes it possible to follow the extent of the reaction and to calculate equilibrium constants (1,2).

B. Indicator methods have been employed extensively for determination of both acid and base strengths in a wide variety of solvents.

If HA represents the acid form of an indicator and B, some base, the equilibrium constant for their interaction can be represented by the expression:

$$K = \frac{K_{BH}}{K_{HA}} = \frac{C_B \times C_{HA}}{C_{BH} \times C_A}$$

where K measures basicity and depends upon the comparative strength of the acids HA and BH. Since the two forms of the indicator, HA and A, possess different colors, adjustment of the relative amounts of B to its conjugate acid BH to produce a certain indicator color, allows evaluation of K.

This method has been employed for determinations in chlorobenzene (3,4), anisole (4), actonitrile (5), benzene (6,7), nitrobenzene (8,9), and chloroform (10).

C. Potentiometric methods have been used recently in the study of the interaction of strong acids with amines. Fritz (11, 12) has found that amines can be titrated quantitatively with strong acids in acetonitrile employing glass and calomel electrodes. The millivoltage reading at half-neutralization, $E_{\frac{1}{2}}$, can be correlated with the base strength of the amine.

Hall (13) used this method for an extensive study of base strengths in ethyl acetate, acetonitrile, nitrobenzene, dichloroethylene and nitromethane. He observed reproducible half-neutralization millicoltage readings after careful standardization of electrodes. The voltage readings were found to be directly proportional to log [BH] / [B]. The mid-point of the titration curve was taken as a measure of the dissociation constant of the amine. Benzene, anisole, dioxane, chloroform and methylene chloride were also studied; however, these gave drifting millivoltage readings for titrations. The titrant acids were perchloric, p-toluenesulfonic and perfluorobutyric, all in dioxane solution.

III. Relative Base Strengths of Amines in Water and Organic Solvents

In the past claims have been made (14,15) that the true order of base strengths for alkyl amines should be $NH_3 < RNH_2 < R_2NH < R_3N$, because of the increasing electron supply to the nitrogen atom by the alkyl groups. In Hall's study the sequence in nitrobenzene and acetonitrile was found to be $NH_3 < RNH_2$, $R_2NH > R_3N$ which is also the order for aqueous solutions (16). Hall concludes that this order of base strength towards the proton is determined solely by some property of the molecules themselves. H. C. Brown's (17) B strain hypothesis is offered in support of such a conclusion.

The base strengths of meta and para substituted anilines show the same base order both in non-protolytic solvents and in water; the effect of substituents is given by the following order: $p\text{-}OCH_3 \approx p\text{-}CH_3 > p\text{-}H > p\text{-}Br > m\text{-}NO_2$. A linear relationship was found between the Hammett σ value of the substituent and $E_{\frac{1}{2}}$, indicating that the glass electrode is actually measuring the H^+ activity in such solutions.

Plots of $E_{\frac{1}{2}}$ (from Hall's data) versus pK_a values of amines in water solution show that fairly good linear relationships hold. It may, therefore, be concluded that the base strength of an amine in water is, broadly speaking, a reliable index of its base strength in organic solvents. Differing degrees of solvation do exist, but they are not important enough to cause major disturbances in the order of base strength.

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Structures of Compounds Containing $(S)_n$, $(Se)_n$, $(S)_n$-Se, and Related Groups

William E. Chambers January 7, 1957

Introduction

The sixth-group elements sulfur and selenium form many membered chains and rings. Besides the S_8 rings of orthorhombic and monoclinic sulfur and the very long chains of plastic and fibrous sulfur, there are polysulfides and polythionic compounds with six or more sulfur atoms in the molecule. Selenium occurs in Se_8 rings in the monoclinic form and as infinite spirals in the hexagonal state; polyselenide anions up to and including hexaselenide appear to exist.[1]

The arrangement of the sulfur atoms in the higher polysulfides has long been debated. Most of the physical evidence has favored a non-branched chain arrangement of the sulfur atoms. Conclusions drawn from characteristic Raman frequencies of trisulfides indicate the non-branched structure.[2] Similar conclusions were reached by electron diffraction studies of dimethyl trisulfide[3] and x-ray investigation of 2,2' diiododimethyl trisulfide. Ultraviolet absorption spectra investigations of diphenyl tetrasulfide and dicyclohexyl hexasulfide also provide strong evidence of non-branched chains of sulfur atoms.[4]

Sulfur may be expected to add to an atom A to form a Coordinate bond $>A\rightarrow S$ or $\rightarrow A\rightarrow S$ only in cases where A is the less electronegative element since such a bond implies that sulfur becomes the negative end of the polar bond. In the case where A is sulfur, a stable coordinate grouping (as above) is accordingly pro-

bable only if the atoms or groups X, bonded to A are able to decrease the effective electronegativity of A to a sufficient degree. A coordinate bond implies that A imparts a negative charge to sulfur and itself acquires a positive charge. The energy required to produce this dipole must oppose the energy of the bonds (electrostatic and single covalent) thereby made possible, and unless the energy producing the dipole is substantially lowered through a favorable electronegativity difference between sulfur and the donor, it is apt to reduce the strength of the resulting bond considerably. Even if the acceptor is more electronegative than the donor, there is no resultant electrostatic strengthening of the bond. Thus, when the participants in a coordinate bond have the same electronegativity, it is not surprising that the bond is too weak for a stable compound to exist.

A double bond $>A=S$ where A is sulfur requires an expanded valence shell of A. There are indications that the divalent sulfur of thioacetals is able to expand its valence shell for hyperconjugation with the carbon atom already bonded to the sulfur atom. In oxygen compounds, like thionyl chloride, sulfoxides, sulfones, and sulfur-oxy ions, sulfur does seem to form partial double bonds and thus to exceed the octet. Fluorine also enables sulfur to exceed the octet, as in sulfur hexafluoride. Thus, the evidence indicates that sulfur expands its valence shell for bonding to additonal atoms only when already bonded to strongly electronegative elements, like oxygen and fluorine or when the new bond is formed by such atoms.

Chemical reactions of a series of polythionic compounds $S_n(SR)_2$ have shown that a divalent sulfur atom forms a bridge between the thio sulfur atoms of two thio groups. Therefore the compounds are built up of unbranched sulfur chains.[5] The unbranched sulfur chain formulated for the polythionic acids[6,7] has been substantiated by radioactive tracer experiments[8,9], and by crystal structure studies[19]. In the reaction of sulfite with polythionates, trithionate and thiosulfate are obtained as products, or in the case of organic polysulfides, disulfide and thiosulfate are obtained. Formerly it was thought that sulfur atoms so easily removed must be bonded differently from the others; hence they could not be part of an unbranched chain. Reactions of compounds containing unbranched sulfur chains with sulfite and cyanide are explainable on the basis of an ionic displacement mechanism. The first step in the reaction is attachment of a sulfite group to one end of a sulfur chain. This might take place as a consequence of an ionic opening of the 8-member ring of rhombic sulfur or as an ionic displacement by sulfite. The next step involves successive ionic displacements of thiosulfate by sulfite. Finally the reaction ends with the formation of trithionate (disulfide in the case of organic polysulfides).

In order to understand the stability of the S_8 molecule, one must consider the forces determining the orientation around the S-S single bond. In the molecule H_2S_2, the bonds formed by the sulfur atoms involve mainly 3p orbitals. The dihedral angle between the planes H-S-S and S-S-H is determined principally by the repulsion of p electrons. Repulsion is a maximum when the p

orbitals of the two sulfur atoms are in the same plane and falls to zero when these orbitals are in orthogenal planes. The theory predicts a skew configuration (that is a configuration where one of the atoms is twisted out of the plane of the rest) with a dihedral angle equal approximately to 90°. From the fact that the similar molecule H_2O_2 and others, such as S_2Cl_2, and dimethyl-trisulfide have dihedral angles on the average nearer 100°, Pauling has concluded that the normal dihedral bond angle for the S-S bond is in the neighborhood of 100°. The increase over the 90° of theory may be due to van der Waals repulsion of non-bonded atoms and to other interactions such as electrostatic interactions of multipoles. The S-S-S bond angle of S_8, which has the staggered configuration, has been found to be 105° with dihedral angle of 102°. This value is close to that which according to Pauling's argument minimizes the energy of the X-S-S-X group. This may explain the stability of the S_8 molecule relative to other sulfur molecules.

The standard state of Se is the d-hexagonal crystalline state in which there are infinite spiral molecules of selenium atoms, with Se-Se-Se bond angle of 105°. A less stable red crystalline state containing Se_8 molecules also exists, and selenium vapor consists of Se_8 and Se_6 molecules, and at higher temperatures, of Se_2 molecules. The spiral molecules in the hexagonal crystals of Se have a three-fold axis. The bond angle is 105°, and the dihedral angle is nearly the same for the three-fold axis as for the 8-membered staggered ring. The greater stability of crystals containing the three-fold spiral for Se is presumably due to the

strong interaction between neighboring molecules, which is made evident in the semi-metallic properties of the crystals. The failure of oxygen to form a molecule such as O_8 is of course due to the greater stability of the multiple bond in the O_2 molecule.

Fibrous sulfur, made by stretching the rubbery form of sulfur obtained on cooling liquid sulfur, does not seem to contain spirals with three-fold axis like Se. On the basis of calculations, a two-turn spiral containing seven atoms as the repeating unit most closely fits the crystal structure measurements.[10]

Dipole moment measurements of a series of di- and tri- sulfides gave values which are consistent with the non-branched chain structure. If branched chains existed, one would expect the coordinate linkage to give a high dipole moment. Dipole moments for methyl-, ethyl-, and propyldisulfide (1.96×10^{-18}) agree quite closely with that for methyl trisulfide (1.67×10^{-18}). The lowering is due to steric hindrance, which prevents the methyl groups from occuping the <u>cis</u> positions.[11]

Rotational isomers of unbranched, non-planar pentathionic compounds have been reported. The non-planarity of the sulfur chain is principally due to the mutual repulsion of the unshared p electron pairs of neighboring sulfur atoms. The barrier restricting rotation about the S-S bond is estimated at 5 k cal. per mole. In the pentathionic compound where the terminal sulfur atoms are rotated to an angle of 90° out of the plane of the three middle atoms, both <u>cis</u> and <u>trans</u> isomers are possible.[12]

Considerations of the actual structure of di-, tri- and tetrasulfide have been offered on the basis of dipole moment measure-

ments. In n-hexadecyl disulfide, the co-planar and freely-rotating structures may be eliminated as possibilities in favor of the skew configuration on the basis of dihedral angle and the moment of the alkyl-sulfur link. Since two non-superimposable mirror-image forms of the same moment can be formulated, it should be possible to resolve the disulfide into two optically active forms. For a trisulfide molecule, three fixed non-planar configurations have been suggested on the basis of some calculations. It is thought that the observed moment of the compound is a combination of the individual moments of the three configurations. In the case of the tetrasulfide, six non-superimposable forms were postulated.[13]

Feher and coworkers have prepared and studied numerous polysulfide compounds of the types S_xCl_2, S_xBr_2, H_2S_x, Na_2S_x, K_2S_x (where x may be 1,----?), as well as Rb_2S_3, Rb_2S_5 and Cs_2Sy (y equal to 2, 3, 5, 6). From considerations of molecular volume and parachor, they have suggested that in all of these the S atoms of the chain are equivalent and that the chain is a non-branched structure.[14-18]

Foss has perhaps provided the most conclusive proof of the structures of polysulfide and polythionate as well as of similar selenium and tellurium compounds by use of the powerful tool of x-ray. Fourier analysis and electron density maps not only show the non-branched chain structure of the sulfur atoms, but also provide a picture of the actual structure of the individual ions and molecules.[19-30]

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THE STEPWISE FORMATION OF METAL COMPLEXES

Robert F. Scarr January 9, 1958

INTRODUCTION

The formation of metal complexes in solution is a stepwise process entailing competition between solvent and ligand molecules for positions in the coordination sphere of the metal ion. The mechanism for formation of complexes in this manner has been discussed by Basolo, et al (3), and by Brown, et al (5, 5a, 5b). A general expression for complex formation between $M^{+\nu}$ and $A^{-\pi}$ is given by:

$$MA_n^{\nu-n} + A^{-\pi} \quad MA_{n+1}^{\nu-(n+1)\pi}$$

Neglecting ionic charge the equilibrium (formation) constant for this step is given by the expression:

$$k_{n+1} = \frac{(MA_{n+1})}{(MA_n)\ (A)}$$

MEASUREMENT OF FORMATION CONSTANTS

Where the stepwise formation of complexes of a metal $M^{+\nu}$ and a ligand $A^{-\pi}$ results in species which are stable over a wide range of ligand concentration and which are reduced reversibly, potentiometric or polarographic methods have been used to determine the formation constants, k_n (12). For cases where the existence of successive complexes overlaps considerably, mathematical treatment of polarographic data permits calculation of k_n. DeFord and Hume (6) have shown that since the shift in half wave potential due to complexation is related to a polymonial in ligand concentration, values of the polynomial may be calculated and plotted against concentration and the curve extrapolated to the intercept to give k_n which is defined as $(k_1 \cdot k_2 \cdot \cdot k_n)$. Repetitive treatment yields individual formation constants.

A method more generally applicable is based on work of J. Bjerrum (4). For cases where overlap is minimal, k_n is given by the reciprocal of the ligand concentration at which the concentrations of MA_n and MA_{n-1} are equal. In more complicated instances, a method of successive approximation may be used to obtain k_n.

FACTORS INFLUENCING RELATION OF SUCCESSIVE FORMATION COMPLEXES (4)

The log of the ratio of successive formation constants depends on the sum of a statistical effect and a ligand effect which is in turn the sum of an electrostatic effect and a "rest" effect. The electrostatic effect is related to the work involved in bringing charges species together. The rest effect includes contributions from steric factors and polarization.

HOW DISTRIBUTION OF SYSTEM IS FOLLOWED

The distribution of successive complexes in a system may be expressed graphically by f-curves where the fraction of the total of a given complex is plotted against ligand concentration for all complexes formed.

Spectrophotometric methods based on Job's principle of continuous variation may be used to obtain these curves by measuring the increase in optical density of the complex over that of the metal ion at a given wavelength with respect to the mole fraction of ligand. Solution of simultaneous equations in a form derived by Katzin and Gebert (10) for several wavelengths leads to determination of the concentrations of individual complexes.

BEHAVIOR OF A SYSTEM OF STEPWISE COMPLEXES

Crystal field theory predicts that if the ligands in the coordination sphere of a metal ion are replaced by ligands of greater perturbing effect, spectral absorbtion peaks are shifted toward the shorter wavelengths. Relative field strengths of various ligands are (13, 14):

$$I^- < Br^- < Cl^- \sim OH^- < F^- \sim H_2O < py < NH_3 < en < \underline{o}\text{-phen} < CN^-$$

Thus replacement of H_2O with ethylenediamine on Ni(II) shifts the absorbtion peak to a lower wavelength (2); with Cl^- on Co(II) the absorption peak is shifted to a higher wavelength (11).

Stepwise formation is important in interpreting ion-exchange data since resin adsorption cannot take place unless an anionic complex (with anion exchangers) is formed within the resin phase. This neccessitates presence of neutral or anionic complexes in the aqueous phase. Herber and Irvine (7) have found only Ni^{++} and $NiCl^+$ to be present in aqueous nickel-chloride systems up to 11 $\underline{M}$ Cl^- thus providing insight into the lack of Ni(II) retention on anion exchangers. Similarly the ion exchange adsorption of Co (II) has been shown (8) to be due to the neutral complex $CoCl_2 \cdot nH_2O$. The anion exchange behavior of Au (III), Be (III), Ag (I) etc., is probably due to resin invasion by anionic complexes, either as ion pairs or weak electrolytes. Jones and Penneman (9) obtained spectra of the actual resin phase showing $Ag(CN)_2^-$ adsorption even though none was present in the aqueous phase at high CN^- concentrations.

Migration studies of Fe (III) fluoride complexes by Babko and Kleiner (1) have verified their own prediction of the ranges of ligand concentration in which ionic complexes of positive or negative charge sign, respectively, are formed.

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The Photochemical Separation of Isotopes

S. C. Chang January 14, 1958

For many purposes of research and practical application, a separation of the natural mixture of the isotopes of an element into its individual constituents is desired. It is true that the Mass Spectrometer (1) can provide a complete separation in ideal cases, but usually the yields are too small for practical purposes. The Gaseous Diffusion method (3) was found to be very successful for the lighter elements; isotopic separation for D, Ne, C, N has been achieved with high states of purity for the individual isotopes by the low-pressure multiple-diffusion method (4). However, low pressures limit the quantities of material which can be prepared. Chlorine, oxygen and helium isotopes have been separated by the Thermal Diffusion (5)(6) method, but efficiency based on power input is very small. Many other methods of separation based on the mass differences of isotopes of a given element have been studied. Among these are the Centrifugal method (7), the Distillation method (8)(9), and the Ion Migration (10)(11) method. Usually these require very high power input for low yields of separated nuclides. In the Electrolytic method (12) for hydrogen isotope separation, the quantity of deuterium was observed to be greater in electrolytic hydrogen cells than in ordinary water, when water is electrolyzed under suitable conditions. The lighter hydrogen isotope is liberated about six times more readily than the heavier one, and thus this procedure provides a very effective method for the separation of very light isotopes. However, the procedure has not proved very successful for other elements.

Exchange Reaction methods (8)(13)(14)(15) have been studied for the concentration of isotopes of quite a large number of elements. This method has the advantage that it can usually be combined in cascade series to increase separation factors markedly. A number of isotopic separations based on the slight differences in reaction rates or decomposition rates of certain suitable compounds are described in the literatures (27,28,29,30).

Photochemical Separation of Isotopes

The first attempt to separate isotopes by a photochemical method was undertaken by Zuber in 1936 (19). He used Hg^{200} and Hg^{202} monoisotopic emmission lines (21) at 2537A to irradiate a Hg vapor-air mixture. After a period of irradiation, some mercury oxide had formed on the walls of the original reaction vessel. Zuber reported a partial enrichment of some of the isotopes in the compounds.

1) Fundamental Principles: In order to enrich a particular Hg isotope, three principles must be considered. Firstly, the absorption spectra of either the individual isotope itself, or some compounds containing the isotopes, should be different for the two isotopes at some wavelengths. Secondly, a light source must be found with sufficiently narrow spectral band width, so that it will excite only one particular isotopic species. Thirdly, a reaction of the excited atom or molecule must be found in which the excited species will react and the unexcited species will not react. Mercury is peculiarly suitable for preliminary investigation, due to the fact that reaction to a various simple solid product is photosensitized.

The resonance line at 2537A emitted by a cool, low-pressure discharge in natural mercury (Hg^N) is composed of a number of hyperfine lines as listed in the table. The small contribution from Hg^{196} is neglected. Lines III and IV consist of single components, while lines I, II and V are complex. It is obvious that the separation should be much more effective for Hg^{200} and Hg^{202} than the other isotopes. However, Hg^{198} had been concentrated by a Hg^{198} monoisotopic source even though the line is not single component.

Table
Hyperfine Structure of
the 2537A line of Hg^N (26)

Lines	Displacement from III(X-200) mA
I (199B,201C)	-25.4
I (199B,201C)	-24.8
I (199B)	-24.60
I (201C)	-28.3
II (X-198,201b)	-9.75
II (X-198,201b)	-9.80
II (X-198)	-10.20
II (X-198)	-9.9
II (201b)	-8.95
III (X-200)	0.0
IV (X-202)	11.5
IV (X-202)	11.50
V (199A,201a,X-204)	21.5
V (199A,201a,X-204)	22.25
V (199A)	22.40
V (199A)	22.80
V (201a)	21.15
V (X-204)	23.10

2) Results in Enrichment

a) Concentration of Hg^{198}: In Billings' work (22), water vapor and Hg^N vapor were passed in a stream of N_2 over a Hg-198 electrodeless resonance lamp. Here the excited atoms were primarily the 198 isotope. The excited Hg atoms together with the substrate gases were led through a thermal precipitator and the HgO deposited on its walls. This deposit was removed and analyzed. The results showed that Hg^{198} was enriched by a factor 1.5 on its natural abuncance. The suggested reaction mechanism can be represented as follows:

$$Hg^* + H_2O \rightarrow HgH + OH$$

$$HgH + OH \rightarrow HgO + H_2$$

The products of reaction are found to contain O_2 in addition to H_2. The following steps lead to the production of O_2:

$$HgO + hV \rightarrow Hg + O$$

$$O + O + M \rightarrow O_2 + M$$

$$OH + OH \rightarrow H_2 + O_2$$

Obviously this will reduce the over-all yield of product HgO.

b) Concentration of Hg^{202}: Zelikoff, et. al., (24) enriched Hg^{202} by employing the method of Billings, et. al. The highest enrichment factor obtained by various experimental conditions was about 1.2. The enrichment of Hg^{202} has also been studied very recently by Osborn, et. al., (25). Isotope Hg^{202} in natural Hg was excited by using a well-cooled arc source operating at the minimum power level consistent with steady radiation output. Various foreign gases, such as hydrogen, methyl,chloride, and isopropyl chloride were added for irradiation with Hg-vapor.

c) Concentration of Hg^{200}: Little work has been done for the concentration of Hg^{200} besides the early work of Zuber's.

3) <u>Factors Concerning Enrichment</u>: The absorption of the monoisotopic radiation by natural Hg is a function of (a) absorption path length, (b) the concentration of Hg in the absorption cell, (c) the pressure of certain foreign gases in the absorption cell, (d) the operating temperature of the lamp, and (e) the type of excitor used with the lamp.

4) <u>Conclusions</u>: Large enrichment of Hg isotopes can be obtained by a single-pass method of the photochemical technique. The working procedure and apparatus are comparatively simple. However, only those isotopes of a particular element which satisfy the previously cited three principles, can be separated by this method.

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THE HYDROGEN BOND - MODERN THEORY

Wallace Cordes February 18, 1958

A. Introduction

The hydrogen bond (hereafter referred to as the H-bond) has been the subject of many studies and speculations since the concept was first introduced by Rodebush and Latimer in 1920 (1). An H-bond can form between two electronegative atoms, usually between two of the following elements: fluorine, oxygen, nitrogen, or carbon. The tendency of these elements, when linked to a hydrogen atom, to form an H-bond increases with increasing electronegativity (2). Small size is also required of the electronegative elements. Although nitrogen and chlorine have the same electronegativity, nitrogen is smaller and participates more readily in an H-bonding interaction (3). Only hydrogen can serve as a link between two electronegative elements due to its extremely small atomic radius (.3Å) and its lack of inner shell electrons (4).

The term"H-bond" has been criticized by some who prefer the designation "H-bridge". The difference in terminology arises from the fact that the energies accompanying this association are small (~ 6 kcal.) in comparison to ordinary covalent bond energies (~ 100 kcal.).

Type of bond	O-H...O	C-H...O	C-H...N	N-H...O	N-H...N	N-H...F	F-H...F
Approx. energy kcal/mole	6	2.6	4.7	2.3	6	5	7

Although its energy is small, the bond is still the strongest intermolecular force known (5). In the general case A-H...B, the strength of the H-bond between A and B is naturally influenced by the other groups which are attached to A and B. The greater the polarity of A-H and/or the greater the effective negative charge on B, the stronger will be the bond (5,6). One of the strongest H-bonds between two given elements is the bond which occurs when the elements form an H-bonded chain structure such as ...A-H...B-H...

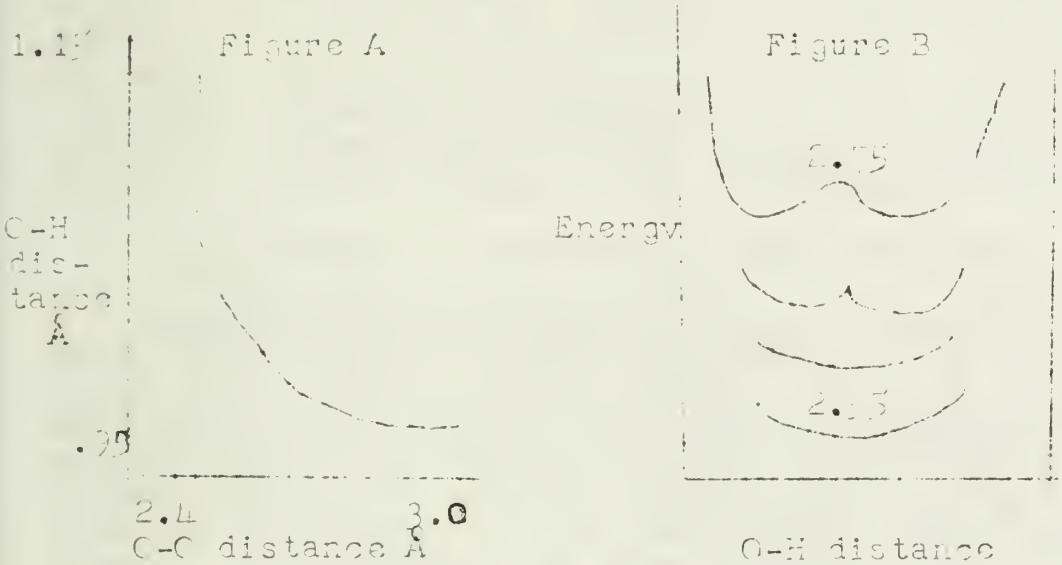
B. Types of H-Bond

H-bonds can first be classified as either intramolecular or intermolecular. The former entails stabilization within a molecule; the latter characterized association between molecules. Both inter- and intramolecular H-bonds are sometimes arbitrarily distinguished as "long" or "short" on the basis of the overall bond length. These

designations are frequently used for the O-H...O, where the O-O distance may vary from 3.30Å to 2.44Å.

A distinction is often made between "straight" and "bent" H-bonds. Most H-bonds are linear; the bifluoride ion, however, is almost triangular (7). The directional properties of lone pair electrons account for many of the deviations from linearity.

Another distinction was at one time made between symmetrical and unsymmetrical H-bonds. It was assumed that the hydrogen atom might be either exactly midway between the two electronegative atoms or close to one of them. The former was called the true H-bond; the latter, the hydroxyl bond (6). This distinction is no longer recognized. It has been shown that the O-H bond distance varies with the O-O separation in the O-H...O bond, as shown in Figure A (8).



This is also reflected by the potential energy curve for hydrogen in the H-bond in Figure B (8). Only at a sufficiently short O-O separation (2.45Å or less) will the hydrogen atom be located exactly between the oxygen atoms. Only two cases of symmetrical H-bonding are known, nickel dimethylglyoxime (O-O distance 2.44 Å) and HF_2^- (2.26 Å).

C. Evidence of Formation - Methods of Detection

Formation or existence of an H-bond can be detected in various ways. Of the following detection methods, the first two are the only direct approaches; the others are based on a comparison of properties of H-bonded groups to similar groups incapable of H-bonding.

1) Crystal Structure Determinations (10)

The H-bond in crystals can appear as finite groups (HF_2^-), infinite chains (HCO_3^-), infinite layers (boric acid), or infinite three dimensional networks (ice) (7). The A-B distance in simple crystals can be calculated from information given by x-ray diffraction. An abnormally short distance between two electronegative atoms indicates the presence of an H-bond. Recent work shows that the effective center of the electron clouds can also be calculated from x-ray information. Relationships have been developed between the A-B bond distance and the A-H I.R. frequency shift, the A-H bond

distance, the A-H...B bond energy, and the A-B force constant for numerous H-bonds (11,12).

2) Electron Diffraction Studies (9,10)

Some attempts have been made to measure directly the positions of the atoms involved in the H-bond by electron diffraction. This method can be carried out only on gases at low pressures. Few H-bonds remain intact under these conditions; the method has been useful only for hydrogen fluoride.

3) Association Phenomena

The intermolecular association caused by H-bonding is reflected by lowering of volatility, melting point, and by an increase in the boiling point, in molecular weight, sublimation energy, and vaporization entropy (because ordering in the liquid states lowers the entropy of this phase) (8), and by an increase in conduction by the chain mechanism (5). Care must be taken in relating H-bonding to the dielectric constant (6). Association may yield linear polymers with a greatly increased dielectric constant, or cyclic polymers with a very small dielectric constant.

4) Effects on Electronic Transitions (13,14)

Formation of an H-bond with the non-bonding (lone pair) electrons of an element lowers the energy of the non-bonding orbital by an amount equal to the H-bond. If one of these non-bonding electrons now is excited to a sigma anti-bonding state, the remaining lone pair electrons cannot sustain the H-bond. After the H-bond breaks, the energy of the excited state is approximately equal to the energy of the same excited state in the absence of the H-bond. The magnitude of this so-called "blue" shift in electronic absorption is therefore of the same order as the energy of the H-bond formed. Thus H-bonding causes a unique upward shift in absorption for the $n \rightarrow \pi^*$ transition as the dielectric constant of the solvent is increased.

5) Infra Red Changes

a. Shift in the A-H stretching band to a lower frequency. A downward shift of the stretching frequency is caused by the reduction of the restoring force of the normal A-H bond due to the attraction of the acceptor atom of the bridge. Examples of the lowering caused by H-bonding are as follows: (8)
Water- vapor 3756 cm^{-1} dil. soln. 3702 cm^{-1} liquid 3455 cm^{-1} ice 3256 cm^{-1}
Methanol- vapor 3682 cm^{-1} dil. soln. 3640 cm^{-1} liquid 3356 cm^{-1}

b. Shift in the A-H deformation band to a higher frequency. The deformation vibration of the A-H group, which is associated with the motion of the hydrogen atom perpendicular to the direction of the bridge, is shifted upward by the attraction of the acceptor atom; for example, in water the frequency of this vibration in the "free" state is 1595 cm^{-1}, and in the liquid state is 1640 cm^{-1}.

c. Broadening of the I.R. bands (15). In weak H-bonds, intermolecular interaction causes an increase in the width of the stretching bands. In strong H-bonds the widening was found to be caused by discreet groups of bands, which originate from the anharmonicity of the bond.

d. Increase in the A-H vibration intensity. H-bonding not only shifts the vibration frequencies, but also causes a marked increase in intensity of the A-H frequency.

e. Downward shift in vibrational frequency on compression. Compression shortens the longer half of the H-bond and thus further reduces the restoring force of the A-H bond.

An interesting application of the matrix isolation method is used to study the I.R. behavior of smaller polymeric units (16,17). Water is dispersed in solid nitrogen (the matrix) at 20°K. This eliminates interfering solute-solvent H-bonding, or low solubility in inert solvents.

D. Formation Theories - Sources of H-Bond Energy

No generally accepted theory on the nature of the H-bond exists today. A short historical resumé of the various explanations which have been proposed follows:

1) Divalent Hydrogen

One of the first theories postulated divalent hydrogen ($O-\overset{-}{H}-\overset{+}{O}$). A number of objections eventually caused abandonment of this idea:

a. The gain in the electrostatic and bond energy is not enough to offset the low electron affinity of hydrogen and the high ionization potential of oxygen.

b. Hydrogen could be divalent only by using 2s or 2p orbitals, which have prohibitive energy requirements.

2) Covalent Resonance

Another misconception which existed for some time involved a resonance of a covalent character.

There is not enough resonance energy possible unless the hydrogen atom is located centrally to the oxygen atoms. This would require too much energy in stretching the normal O-H bond.

3) Electrostatic Attraction

The fact that the H-bond only occurs between two electronegative elements implies electrostatic contributions to the bond.

After the rejection of the above theories and until quite recently such electrostatic attraction was given as the sole basis for the existence of H-bonds. This electrostatic energy can be calculated theoretically by various methods: Assignment of formal charges and summation of Coulombic interactions, representation of water as a dipole and quadrupole and summation of charges, or calculation of charge density. No one as yet has attempted the latter method, but the other calculations and modifications yield consistent values of 6 kcal/mole for the electrostatic interaction. These forces could therefore account for the energy of the H-bond.

There are several inadequacies to a purely electrostatic approach:

a. Electrostatic attraction cannot explain angular H-bonds.
b. Electrostatic bonds can account for only a 30% increase in I.R. vibrational intensity, while 1000% increases are common.
c. No correlation between H-bond strength and dipole moment of the proton acceptor appears to exist.

4) Present Theories

The electrostatic contribution to the formation of the H-bond cannot be ignored. Current theories also include other possible sources of the bond energy: (a) electrostatic energy, (b) delocalization energy, (c) repulsive energy, and (d) dispersion energy.

The fact that (a) can account for the total energy of the H-bond does not eliminate the other possibilities; it simply suggests that the sum of (b), (c), and (d) is zero.

<u>Delocalization Energy</u> (9) The main supporting evidence for the delocalization energy is the large increase in intensity of I.R. absorption due to H-bonding. This implies a larger fluctuation of charge when the H-bond is formed, which is only possible if the charge can move from the farther electronegative atom to the A-H region. Delocalization is also reflected by the enhanced intensity and change of frequency with compression. N.M.R. studies suggest that the electron in the hydrogen atom is also delocalized.

The following resonance forms are possible for O-H...O:

(a) $`O_1\overset{-}{H}...O_2\langle$ Purely covalent, no charge transfer.

(b) $`O_1\overset{-+}{H}...O_2\langle$ Purely ionic, no charge transfer.

(c) $`\overset{+}{O_1}\overset{-}{H}...O_2\langle$ Purely ionic, no charge transfer.

(d) $`\overset{-}{O_1}H \text{---} \overset{+}{O_2}\langle$ Charge transfer, long $H-O_2$ bond.

(e) $`\overset{-}{O_1}\underset{\text{---}}{H} \quad \overset{+}{O_2}\langle$ Charge transfer, O_1-O_2 bond.

Structures (d) and (e) are the sources of delocalization energy.

Using bond lengths and bond order relationships, and considering only forms (a), (b), and (d), Pauling (18) calculated that when the O_1-O_2 distance is 2.8Å, (d) contributes 2% to the total bond energy. When the O_1-O_2 distance is 2.5Å, (d) contributes 10%. The dipole which would be expected when O_2 bonds to the O_1-H region has been detected (19).

Tsumobura (20) included the above five structures in a wave equation and solved it for the O_1-H distance .96Å and the O_1-O_2 distance 2.7Å. The delocalization energy was found to be 8.1 kcal/mole, in agreement with previous estimates. The contribution from (d) was approximately equal to the contribution from (e). One difficulty in these calculations is the choice of the orbital for the non-bonding electron of O_2 and the bonding electron of O_1.

Repulsive Energy Repulsion forces must be considered, since both electrostatic and delocalization forces tend to shorten the total length of the bond. These forces are difficult to estimate, since van der Waal's radii and interatomic distances do not apply to the partially bonded system (9).

Dispersion Forces Dispersion forces arise from non-bonded atoms in the molecules and non-bonding electrons of the bonded atoms (9). Estimates of the value of these forces are obtained through comparison to similar molecules with known van der Waal's forces.

The only H-bonded system which has been studied in any detail is ice, which has a typical "long" H-bond (2.76Å). The estimated contributions are as follows:

Type of Energy	Energy in kcal/mole
Electrostatic	+6
Delocalization	+8
Repulsive	-8.4
Dispersion	+3
Total theoretical	+8.6
Experimental	+6.1

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STRUCTURES OF NICKEL(II) COMPLEXES

TETRAHEDRAL OR SQUARE CO-PLANAR?

M. Kubota February 25, 1958

I. INTRODUCTION

The stereochemistry of coordination number four in nickel(II) is usually approached in terms of the Pauling concept of hybridization of orbitals, the directional properties of these orbitals and their correlation to magnetic behavior (1). Two types of hybridizations appear to be possible in tetracovalent nickel(II), namely, $4s4p^3$(tetrahedral) and $3d4s4p^2$(square co-planar). The square co-planar complex should be diamagnetic, because of the absence of unpaired electrons, while the tetrahedral form should be paramagnetic, because of two unpaired electrons. In the past two decades, the assignment of complexes to the tetrahedral and square co-planar classes has been based primarily on this magnetic criterion.

Considerable research interest in the proposed configurations has been inspired by the absence of unequivocal experimental proof for the existence of tetrahedral configuration in nickel(II) complexes (2). Recent reports based on quantum mechanical considerations (3), electron diffraction studies (4), x-ray crystallography (5), dipole moment data and absorption spectra (6), indicate that the square co-planar configuration can be assumed by <u>paramagnetic</u>, as well as diamagnetic complexes. Furthermore, magnetic susceptibility data, reflection spectra (7) and absorption spectra (8) suggest that many apparently tetrahedral complexes are in reality octahedral. Convincing evidence has thus been obtained to demonstrate that the magnetic moment is <u>not</u> a reliable criterion for bond type or configuration in tetracovalent nickel(II) complexes. Evidence for the tetrahedral configuration is weak and even suggests "non-existence".

II. DIAMAGNETIC COMPLEXES. THE SQUARE CO-PLANAR CONFIGURATION

The diamagnetic complexes are usually yellow to red or brown, in contrast to the paramagnetic complexes which are generally blue or green. The absorption spectra should be a better criterion, and indeed, the diamagnetic complexes exhibit sharp, intense bands in the vicinity of 4000Å (9). The configuration of diamagnetic complexes is believed to be square co-planar on the basis of the following evidence.

1. X-ray diffraction: Abundant support for square co-planar disposition of bonds in diamagnetic nickel(II) complexes has been provided by studies on numerous complexes. (e.g., $K_2Ni(C_2O_2S_2)_2$, $BaNi(CN)_4 \cdot 4H_2O$) (9).

2. Dipole moments: Since the moments of some diamagnetic complexes are zero, it must be concluded that they are <u>trans</u> co-planar. (e.g., $NiCl_2 \cdot 2Et_3P$) (9).

3. Cis-trans isomerism: Isolation of isomeric forms of several diamagnetic complexes has been accomplished. (e.g., complexes with monoethylglyoxime, benzylmethylglyoxime and salicylaldimine (9).

4. Theoretical: Diamagnetism infers pairing of d electrons, thereby permitting $3d4s4p^2$ hybridization, which characterizes square co-planar configurations, such as in platinum(II) complexes. The ligand field theory also predicts a square configuration in the spin paired case.

III. PARAMAGNETIC COMPLEXES. THE TETRAHEDRAL CONFIGURATION?

The paramagnetic complexes have magnetic moments between 3.2 to 3.4 BM, which indicates the presence of two unpaired electrons. Arguments in support of Pauling's prediction that the paramagnetic complexes would be tetrahedral can be summarized as follows.

1. Theoretical: Since $4s4p^3$ orbitals are the first empty orbitals available for bonding, one would expect sp^3 hybridization as in tetrahedral carbon, zinc(II) and copper(I). This assumption loses force, if one considers complexes of copper(II), where the configuration is usually square co-planar (9).

2. Fine structure of K x-ray absorption edge: Absence of peaks which characterize 1s to 4p transitions in bis(salicylaldehyde)-nickel(II) supports sp^3 type bonding (10).

3. Dipole moments: A value of 8.85 D for the paramagnetic complex $Ni(NO_3)_2 \cdot 2Et_3P$ excludes the trans-planar configuration, but is compatible with a tetrahedral or cis-planar (9).

4. X-ray diffraction: The x-ray pattern of anhydrous bis(salicylaldehyde) nickel(II) is almost identical with the analogous zinc (II) compound, but is entirely different from the copper(II) compound. Zinc(II) complexes have been shown to be tetrahedral, while the copper(II) complexes planar (11).

IV. RECENT STUDIES ON TETRACOVALENT NICKEL(II) COMPLEXES

Of most significance in recent years, is the demonstration that some paramagnetic complexes have square co-planar, instead of the expected tetrahedral configuration. Quantum mechanical calculations by Hartmann and Fischer-Wasels (3) have shown that paramagnetic complexes with square co-planar structures should be possible. This conclusion has been verified by electron diffraction studies on paramagnetic bis(acetylacetone) nickel(II), which indicate that the free molecule has a square co-planar structure (4). X-ray diffraction patterns of this compound show that three nickel atoms are nearly co-linear, with adjacent nickel atoms separated by 2.72 and 2.8 Å. The proximity of the nickel atoms implies that the crystals must contain trinuclear molecules (5).

The magnetic susceptibilities of a series of nickel(II) complexes of N-alkylsalicylaldimine in chloroform and benzene range from 0.29 to 3.16 BM. After applying suitable corrections for

atomic polarization, it was shown that the above solutions have dipole moments of approximately zero (6). This is compatible only with a trans-planar configuration. The absorption curves in benzene at different temperatures indicate equilibrium between two differently absorbing species. A low intensity absorption band at 610 to 640 m is typical of forbidden 3d-3d transitions, and has been taken as evidence for unoccupied 3d levels in such solutions. On the basis of this information, the investigators conclude that equilibrium is not between planar and tetrahedral forms, but probably one between inner orbital $3d4s4p^2$ and outer orbital $4s4p^24d$ complexes (6). Exchange studies with radio nickel (12) and tagged ligand molecules (13) apparently support this proposal.

The equilibrium between yellow (diamagnetic) and blue (paramagnetic) nickel(II) triethylenetetramine ions in solutions at different ionic strength has been studied by observing the changes in intensity of the absorption band at 443 mμ. An equilibrium between blue cis- or trans-octahedral complex NiA_4X_2 and yellow square co-planar complex NiA_4 (where X is solvent or anion group and A is ligand) has been postulated (8).

Comparison of the magnetic moments (7,14) and reflection spectra (7) of some apparently tetrahedral complexes with values of known octahedral complexes indicate that most of the complexes studied are actually octahedral.

Lions and Martin (15) report that the ligand 2,2' salicylideneamino-diphenyl which cannot be strainlessly disposed in a square co-planar arrangement cannot normally coordinate with nickel(II).

The absence of conclusive evidence for the existence of tetrahedral nickel(II) complexes can be explained on the basis of crystal field considerations. Gillespie and Nyholm have pointed out two requirements which must be met in order for a complex to be tetrahedral: first, a ligand which is readily polarized and secondly, a non-bonding electron shell, which is symmetrical with respect to four tetrahedrally disposed ligands (16). Tetrahedral symmetry in nickel(II) is not expected, due to the Jahn-Teller effect (17). It should be noted that the existence of paramagnetic square co-planar nickel(II) complexes can be explained by ligand field theory. In the presence of a weak field, the $d_{x^2-y^2}$ orbital can be available for non-bonding electrons (2).

V. FACTORS WHICH INFLUENCE THE TYPE OF COMPLEX FORMED

Whether a tetracovalent nickel(II) complex is paramagnetic or diamagnetic, depends not only on the nature of the ligands, but also on the environment. The following factors must be considered.

1. "Strong" ligands which can exert a strong crystal field would tend to give diamagnetic complexes. The possibility of double bond formation would favor the diamagnetic square arrangement, since effects of pi bonding should shorten the ligand distance, hence increase the crystal field (17).

2. If the coordination number remains the same, increases in temperature should reduce the ligand field and hence favor the paramagnetic form. Thus the green complex $Ni(NO_3)_2 \cdot 2Et_3P$ is paramagnetic at room temperature, but an alcoholic solution of this complex becomes red when cooled. The temperature dependent equilibrium between paramagnetic and diamagnetic nickel(II) complexes has been studied and thermodynamic properties associated with the process have been calculated (19).

3. Solvation or coordination on the z axis should promote paramagnetism (17). This enables one to account for the following observations:

a. Bis(ethylenediamine)nickel(II) perchlorate is paramagnetic, whereas the pink complex $(Nien_2)(AgIBr)_2$ is diamagnetic in the solid state. The latter compound turns blue-violet and paramagnetic in solution.

b. Bis(salicylaldoxime)nickel(II) is diamagnetic in the solid state and in benzene, but paramagnetic in pyridine (20). Basolo and Matuosh have shown that the coordination number has been expanded to six, by isolation of the paramagnetic complex containing two molecules of pyridine (21). Some complexes such as bis(N-methylsalicylaldimine)nickel(II), which are diamagnetic in the solid state, show paramagnetism even in "non-coordinating" solvents such as benzene or chloroform.

It is apparent that the balance between the paramagnetic and diamagnetic forms is delicately poised, and small structural differences in the ligands and changes in the environment can often result in a change of complex type (22). It should be noted that the amount of energy required to effect pairing of electrons in nickel(II) is approximately 42 kcal. (23).

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The Solvolysis and Solvolytic Products of Transition Metal Halides

Ross Latham, Jr. March 11, 1958

It is well known that $SiCl_4$ undergoes solvolysis with alcohols as well as with water. It has also been shown that certain of the transition metals, particularly those in groups IV b and V b, undergo solvolysis with the replacement of one or more of the halogen atoms by solvent anions. This substitution seems to be limited to halides exhibiting somewhat covalent character. In this way, alkoxides and halo-alkoxides can be formed by reaction of the transition metal halides with alcohol; amides and halo-amides can be formed by reaction with ammonia or amines.

I. Ammonolysis

Of the transition metal halides in group IV b, $TiCl_4$, $ZrCl_4$, and $HfCl_4$ and in group V b, VCl_4 and $NbCl_5$ have shown a tendency to solvolyze. Fowles and Pollard[1,2,3] have studied the ammonolysis of $NbCl_5$, $TiCl_4$, $ZrCl_4$, and $ThCl_4$ and have formulated reaction mechanisms to explain their observations. According to their measurements, the following reactions take place initially:

$$NbCl_5 + 18NH_3 \rightarrow NbCl_3(NH_2)_2 \cdot 8NH_3 + 2NH_4Cl \cdot 3NH_3$$

$$3TiCl_4 + 48NH_3 \rightarrow 2Ti(NH_2)_3Cl + Ti(NH_2)_2Cl_2 \cdot 8NH_3 + 8NH_4Cl \cdot 3NH_3$$

$$ZrCl_4 + 18NH_3 \rightarrow ZrNH_2Cl_3 \cdot 14NH_3 + NH_4Cl \cdot 3NH_3$$

Thorium tetrachloride forms simple addition compounds with ammonia, and does not appear to undergo ammonolysis.

As the reaction products are heated, ammonia is lost in stages until a stable compound is formed. At 160°C, $NbCl_3(NH_2)_2$ can be isolated. Heating at elevated temperatures results in the formation of a nitride of undetermined formula. The titanium tetrachloride ammonolysis is more complicated. The initial ammonolysis product, if subjected to a vacuum at the reaction temperature, loses NH_3, forming a mixture with the empirical formula $TiCl_4 \cdot 8NH_3$. This is thought to be a mixture of $2Ti(NH_2)_3Cl + Ti(NH_2)_2Cl_2 \cdot 8NH_2 + 8NH_4Cl$. Heating this mixture to 90° yields a product of empirical formula $TiCl_4 \cdot 4NH_3$, which is thought to be $Ti(NH_2)_2Cl_2 + 2NH_4Cl$. Continued heating to 180° yields $TiCl_4 \cdot 2NH_3$, which is thought to be $Ti(NH_2)Cl_3 + NH_4Cl$. Heating at 300° leaves $TiNCl$[4]. No evidence for similar intermediates has been found in the decomposition of $ZrNH_2Cl_3 \cdot 14NH_3$. At 180°C, $Zr(NH_2)Cl_3$ can be isolated. At 800° a black substance remains containing no chlorine. With ThI_3 the following reaction[5] is believed to occur:

$$ThI_3 + 5NH_3 \rightarrow ThNH_2I_3 \cdot 4NH_3 + 1/2\ H_2$$

Solvolysis studies have been extended to include the aminolysis of transition metal halides by primary, secondary, or tertiary amines. Dermer and Fernelius[6] report the formation of $Ti(N\emptyset_2)_4$ (which is surprising because of steric strain). Other investigators[7,8] have reported formation of addition compounds of $TiCl_4$ with ammonia and

mono-, di-, and tri methyl amine in the vapor state. They have also observed that Ti(IV) is reduced to Ti(III) with NMe_3. Two different mechanisms are proposed for this reduction.

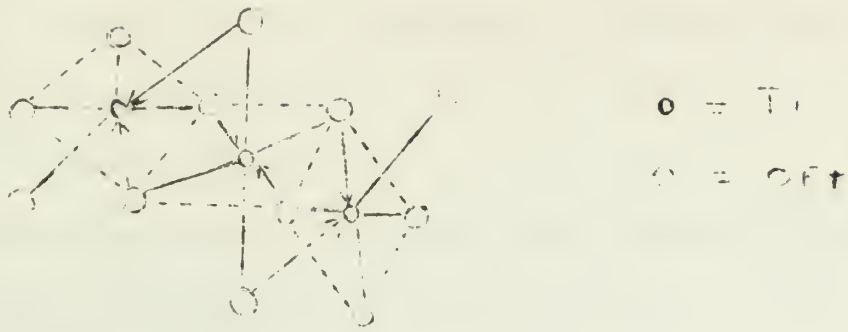
Flowles and Pleass[9,10] have recently made studies of the reactions of VCl_4 and $NbCl_5$ with mono-, di-, and tri-methylamine. At low amine concentrations, 1:1 adducts, $VCl_4 \cdot NHMe_2$ or $VCl_4 \cdot NMe_3$, form; these appear to be thermally stable up to 150°C in the absence of free amine. However, as the amine concentration is increased, HCl is eliminated. Thus for VCl_4, first $VCl_3 \cdot NMe_2$ and then $VCl_3(NMe_2)_2$ is formed. An intermediate in such a reaction is $VCl_3(NMe_2) \cdot NHMe_2$, which splits out HCl. It is suggested that $VCl(NMe_2)_3$ is not formed because of the steric difficulty in forming $VCl_2(NMe_2)_2 \cdot NHMe_2$ as the intermediate. $NbCl_5$ reacts in a similar fashion, giving as a final product, $NbCl_3(NMe_2)_2$. The reaction of VCl_4 with NH_2Me yields $VCl_2(NHMe)_2$: with $NbCl_5$, $NbCl_2(NHMe)_3$ is obtained. Evidence of dimeric and trimeric aggregates is reported. Although no reduction was observed for Nb(V), the reaction of VCl_4 with excess NMe_3 gives as the principle product $VCl_3 \cdot 2NMe_3$.

A paper by Fowles[11] (not as yet available) deals with the reactions of some transition metal chlorides with anhydrous ethylenediamine and proplenediamine.

II. Alcoholysis

The order of ease of hydrolysis for the group IV metal halides has been shown to be $SiCl_4 > TiCl_4 > ZrCl_4 > ThCl_4$. This order can be extended to alcoholysis and ammonolysis reactions as well. $TiCl_4$ reacts readily with ethyl alcohol giving $TiCl_2(OEt)_2$. To prepare the tetraalkoxide, a base such as NH_3 is added to the reaction mixture. In this way, $Ti(OEt)_4$ is prepared commercially. $ZrCl_4$ reacts with ethanol yielding $ZrCl_3(OEt) \cdot EtOH$. This equilibrates with $ZrCl_2(OEt)_2$, liberating HCl. $ZrCl(OEt)_3$ can be formed by the reaction of acetyl chloride with $Zr(OEt)_4$[12]. As in ammonolysis, $ThCl_4$ only forms addition compounds with alcohols, coordinating 4 alcohol molecules[13]. $ZrCl(OCMe_3)_3$, found to be unreactive in so far as no further replacement of chlorine occurs, will react with tertiary alcohols, giving the compound $HOZr(OCMe_3)_3$[14]. Systematic investigation of the primary, secondary, and tertiary alkoxides of titanium and zirconium by Bradley and co-workers[15,16,17] showed interesting properties indicating that intermolecular bonding is present for secondary and primary alkoxides of titanium and zirconium, but not for the tertiary alkoxides. This tendency to dimerize and trimerize has been considered both from the standpoint of comparative electron-releasing tendencies of alkyl groups and from that of steric effects of alkyl chain branching.

More recently, attention has been directed to the polymerized structure of $Ti(OR)_4$[18,19,20] and its solvates, $Ti(OR)_4 \cdot (ROH)_2$. It has been proposed that the alkoxides and amides are not simple monomeric units, but are actually dimeric, trimeric, and in some cases polymeric. A structure such as the one below is suggested for the trimer $Ti_3(OEt)_{12}$.



Although other solvent systems have been studied, such as $POCl_3$, SO_2Cl_2, and PCl_5, no evidence of substitution is presented. Anhydrous HNO_3 reacts with $TiCl_4$, giving a compound of the formula $TiOCl(NO_3)_2$. However, the main solvolytic reactions that have been investigated involve alcohols, ammonia, and the amines.

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ACID-BASE REACTIONS IN ANHYDROUS HYDROGEN FLUORIDE

Ronald O. Ragsdale March 18, 1958

A. INTRODUCTION

Fremy (1) was the first to obtain anhydrous hydrogen fluoride by the thermal decomposition of pure, dry potassium hydrogen fluoride. This method is still used in the laboratory today (2). In 1869 Gore (3) studied the solubilities and conductivities of a few inorganic compounds in hydrogen fluoride. Very little further work was done until 1928 when Fredenhagen and co-workers (4) published the first of a series of papers dealing with the solvent properties of hydrogen fluoride.

B. PHYSICAL PROPERTIES

The physical properties of water, ammonia, and hydrogen fluoride (5) are compared in Table I.

Physical Properties of Water, Ammonia, and Hydrogen Fluoride

	Water	Ammonia	Hydrogen Fluoride
Molecular weight	18.016	17.032	20.008
Melting point (^{o}C)	0	-77.7	-83.1
Boiling point (^{o}C)	100	-33.4	19.54
Equiv. cond. (ohm^{-1})	$6x10^{-8}$	$5x10^{-9}$	$1.4x10^{-5}$ (6) to $2.6x10^{-6}$ (7)
Dielectric constant (E)	81.1	22	83.6
Dipole moment ($Dx10^{18}$)	1.85	1.47	1.9

The liquid hydrogen fluoride resembles water to a greater extent than it does the other hydrogen halides. These anomalous physical properties of hydrogen fluoride can be explained by the results of vapor density determination (8),(9) and electron (10) and X-ray diffraction (11) studies which show that at moderate temperatures HF consists mainly of polymeric aggregates, both in the liquid state and also in the vapor phase. The data appear to fit a picture in which the simple HF units are associated through hydrogen bonding into a zig-zag chain configuration, with an F-H-F distance $2.55 \pm 0.03A^{o}$ and bond angles of 140 ± 5°.

C. SOLVENT PROPERTIES

Liquid HF is a poor solvent for elementary substances. Nonmetals are insoluble with the exception of bromine, which is slightly soluble. Na, K and the alkaline earth metals react with the evolution of hydrogen; the noble metals are relatively unaffected by the solvent.

The dissolution of salts, other than fluorides, is often accompanied by extensive solvolysis.

D. ACID-BASE RELATIONSHIPS

Acidic solvents like HF are usually poor proton acceptors and good proton donors. Perchloric acid is the only known compound which is capable of serving as a Bronsted acid (12).

According to the theory of solvent systems any substance capable of increasing the concentration of the cation of a self-ionizing solvent acts as an acid with respect to that solvent. The ions derived from the solvent itself represent the strongest acid and base for that solvent system. For anhydrous HF, the strongest possible base is the fluoride anion, while the strongest acid will be the ion H_2F^+, called the fluoronium ion.

The autoionization of HF is assumed to take the place according to the equation:

$$2HF \rightleftarrows H_2F^+ + F^-$$

Any soluble ionic fluoride such as NaF will constitute a base (13). Compounds such as nitric acid are basic to hydrogen fluoride (14). Due to solvolysis, even H_2SO_4 acts as a base.

There are, however, a number of derivatives of HF which exhibit acidic behavior in HF, in the sense that they can compete successfully with the proton for a share in the electrons of the fluoride ion and thus increase the concentration of the H_2F^+ ion in solution.

Ex. $BF_3 + 2HF \rightleftarrows H_2F^+ + BF_4^-$

Kilpatrick (15) has found that BF_3 displaces the equilibrium to the right. He proposed the term co-acid for fluoride ion acceptors like BF_3 which increase the H_2F^+ ion concentration.

Qualitatively, for fluorides to compete successfully for a share in the electrons of the fluoride ion, they must fulfill the following requirements:
(a) They must possess a central atom with orbitals available for binding fluoride ions; (b) the valence state of the central atom must be high; (c) the geometrical factors must be such as to permit the central atom to increase its coordination number.

Clifford and co-workers (16) used the following experimental criteria to determine relative acid strengths in liquid hydrogen fluoride.

1. Solubility. Low solubility indicates low affinity for the fluoride ion.
2. Solvent power. The ability of the acids to dissolve metallic fluorides of varying basicity such as (CoF_3, MnF_3, CrF_3), HgF_2, AgF_2 (NiF_2, CoF_2), CaF_2, AgF, and NaF was used as a qualitative measure of the acid strength.
3. Solvent power on various metals. The ability to dissolve metals such as Hg, Ag, Cu, Pb, Sn, Nb, Cr, Zn, Mn, Mg, and Ca was also used as a criterion in setting up a qualitative order for the relative acid strengths of fluoro-acids.

Using these criteria as measures of acid strength, fluoro-acids have been classified in the order of decreasing acid strengths from categories 1 to 7 as summarized in Table II. The detailed experimental observations for the various categories may be summarized as follows:

1. Dissolve CoF_3 2. Dissolve Cr, Mn 3. Dissolve Mg or react with CoF_2, CuF_2, AgF_2 4. Form salt with AgF 5. Very weak (solution unstable) 6. Amphoteric 7. Neutral 8. Soluble strong bases including the fluorides of the alkali and alkaline earths.

Of all the acids investigated, only four namely SbF_5, AsF_5, BF_3, and SnF_4 were found to be capable of dissolving electropositive metals. Argentous salts were prepared from solutions in HF of BF_3, SiF_4, GeF_4, SnF_4, TiF_4, SeF_4, PF_5, AsF_5, SbF_5, IF_5, VF_5, MoF_5, TaF_5, MoF_6, WF_6, and probably ReF_6.

Table II

Relative Strengths of Fluoroacids in Hydrogen Fluoride

Group	Category - increasing acidity →						
	7	6	5	4	3	2	1
II A		Be(II)					
IV A			Ti(IV)				
V A				Nb(V) Ta(V)	V(V)		
VI A		Cr(III)			Mo(VI) W(VI)		
VII A					Re(VI)		
III B		Al(III)				B(III)	
IV B	C		Si(IV)	Ge(IV)	Sn(IV)		
V B	N	Sb(III)			P(V)	As(V)	Sb(V)
VI B	O, S(VI)		Se(IV)	Te(VI)			
VII B	F,Cl(III)			I(V)			

Aluminum (III), Cr(III), Sb(III), and Be(II) fluorides are amphoteric in HF. Aluminum fluoride is quite soluble in HF, but upon the addition of the acid BF_3, AlF_3 is precipitated.

Ex. $Na_3AlF_6 + 3H(BF_4) \rightarrow AlF_3\downarrow + 3Na(BF_4) + 3HF$

Clifford and Morris (17) did some quantitative work on the salts of fluoroacids of P(V), As(V), Ge(IV), Se(IV), Te(VI), and I(V). The study had to be limited to salts of volatile fluoroacids so that the salts could be prepared in the presence of an excess of the acid

and the excess acid subsequently removed by evaporation. The results showed that in this group the relative acid strengths follow the order:
(AsF_5, PF_5), GeF_4, TeF_6, IF_5, and SeF_4.

Pure anhydrous $AgBF_4$ was prepared by precipitation from anhydrous HF solutions of $AgNO_3$ with BF_3 (18).

McCaulay and co-workers (19) evaluated various metal fluorides and other metal salts as acids in the HF system. Vapor pressure measurements of BF_3 (20) in a mixture of m-xylene and HF showed that the xylene reacted with BF_3 to form a 1:1 complex. The extraction of m-xylene from p-xylene was used as a criterion of acid strength. In each test a mixture of m- and p-xylene was treated with HF plus the metal salt. In this medium, a fluoride may act as a Lewis acid and coordinate with a fluoride ion. The proton released then adds preferentially to m-xylene. Four fluorides proved to be strong acids: TiF_4, NbF_5, and TaF_5, and BF_3, whereas PF_5 was found to be a weak acid.

Clifford and Sargent (21) studied the existence of metallic complexes in HF. In most cases the complexes were not sufficiently stable to withstand isolation of solid phases; consequently, conclusions were based on visual observations. Complexes of Co(II), Co(III), Ni(II), Cu(II), Zn(II), Hg(II), and Pb(II) are believed to form. The nickel-acetonitrile complex was studied more extensively by observing the concentration of nickel taken into solution when introduced as a metal powder into HF solutions of known acetonitrile concentration. The ion, $[Ni(CH_3CN)]^{+2}$, was the predominant species, and an instability constant $j = 1.4 \times 10^{-3}$ was calculated.

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THESIS ABSTRACT

OBSERVATIONS ON THE RARE EARTHS: CHEMICAL AND ELECTROCHEMICAL STUDIES OF SOLUTIONS OF RARE EARTH METAL SALTS IN ANHYDROUS DIMETHYLFORMAMIDE

Valentine D. Galasyn March 1958

Solvated rare earth iodides, having the general formula $LnI_3 \cdot 8DMF$, have been prepared by the reaction between the appropriate hydrated rare earth acetate and acetyl iodide in a dimethylformamide medium (Ln represents La, Pr, Nd, Sm, and Gd, whereas DMF represents dimethylformamide). The reaction can be represented by the following equation:

$$Ln(C_2H_3O_2)_3 \cdot xH_2O + (3 + x)CH_3COI \xrightarrow{DMF}$$

$$LnI_3 \cdot 8DMF + 3(CH_3CO)_2O + xHC_2H_3O_2 + xHI$$

The desired product is precipitated from the clear solution of the reaction products by the addition of ether. Continued recrystallization from dimethylformamide is necessary to obtain a pure product.

The neodymium compound has also been prepared by the metathetical reaction between hydrated neodymium chloride and potassium iodide in a dimethylformamide medium. In this method, water is removed from the system by distillation of the benzene-water azeotrope from a mixture of the hydrated rare earth chloride, dimethylformamide, and benzene. The excess benzene is removed by distillation, and the resulting solution is then mixed with a dimethylformamide solution of potassium iodide. The insoluble potassium chloride that forms is removed by filtration, and the desired product is precipitated from the clear filtrate by the addition of ether.

These crystalline compounds are extremely hygroscopic and must be handled under anhydrous conditions. The melting point data suggest that bonding exists between the dimethylformamide molecules and the rare earth cations.

The compound $Sm(C_2H_3O_2)_3 \cdot DMF$ has been prepared by distillation of the benzene-water azeotrope from a dimethylformamide solution of the hydrated acetate. This crystalline compound is not hygroscopic. This method of removing water shows promise as a generally applicable procedure for the preparation of a variety of anhydrous salts.

The absorption spectra of $PrI_3 \cdot 8DMF$, $NdI_3 \cdot 8DMF$, and $SmI_3 \cdot 8DMF$ in dimethylformamide have been obtained. These were compared with the absorption spectra of the corresponding rare earth perchlorates in aqueous solution. Slight displacements in wavelengths, alterations in absolute intensities for certain bands, and changes in resolutions of complex bands were observed. This suggests that a high degree of association exists between the rare earth cations and solvent molecules.

The solubilities of the solvated rare earth iodides in dimethylformamide have been determined quantitatively. The compounds are all highly soluble. The trend in solubilities could not be correlated with cationic radii.

Conductivity studies showed that these salts are moderately weak conductors in dimethylformamide. In concentrated solutions, the conductivities decrease in the series from lanthanum to gadolinium. This corresponds with decreasing cationic radius and increasing degree of cationic solvation.

Various electrolyses were carried out with dimethylformamide solutions of these salts in an attempt to obtain the free rare earth metals. A black cathode deposit was obtained during two electrolyses of solutions of $LaI_3 \cdot 8DMF$. Although the presence of lanthanum metal in these deposits was indicated, it could not be definitely proven. X-ray diffraction analysis was inconclusive.

The exact conditions under which the black deposit formed could not be reproduced again during subsequent electrolyses. The reasons for this are unknown. However, it is felt that the nature of the cathode surface is of prime importance in determining whether the deposit will form. If the exact conditions required are found, the black deposit should be obtainable again.

It appears that solvent decomposition during electrolysis rules out this system as a means of obtaining the pure rare earth metals in usable amounts.

Neodymium amalgams have been prepared by the electrolysis of dimethylformamide solutions of $NdI_3 \cdot 8DMF$, using a mercury pool cathode.

THE STRUCTURE OF GASEOUS ALKALI HALIDES

John G. Verkade March 25, 1958

The increased interest in recent years in the structure of gaseous alkali halides stems from the wealth of information on bonding which can be derived from a study of these relatively simple diatomic systems.

I. The Rittner Ionic Model

The Rittner ionic model[1] of the alkali halides marked the first successful attempt to calculate binding energies and dipole moments on the basis of an equation involving a sum of various interactions which could be directly or indirectly obtained by experiment.

A. Dipole Moments

The dipole moment is of interest in connection with a commonly employed criterion for fraction of ionic character of a bond[2].

$$f = \frac{\mu}{er}$$

This criterion leads to the curious dilemma that the quantity f is experimentally found to be about 0.7 (Cf. table) whereas the bonding is generally supposed to be ionic. The fraction f as given above fails to consider the mutual deformation polarization taking place in the diatomic molecule.

The alkali halides are considered to be constituted of ions each of which is polarized by the electrostatic field of the other.

$$\text{Now: } \mu_{net} = er - (\mu_1 + \mu_2)$$
$$\text{where } \mu_1 = \alpha_1 E_2$$
$$\text{and } \mu_2 = \alpha_2 E_2$$
$$\text{or } \mu_{net} = er - \frac{(r^4 e(\alpha_1 + \alpha_2) + 4r\alpha_1\alpha_2)}{r^6 - 4\alpha_1\alpha_2}$$

where μ_{net} is the net dipole moment, μ_1 and μ_2 are induced dipoles, E_1 and E_2 are electrostatic fields, r is the internuclear distance, and α_1 and α_2 are polarizabilities.

Rittner gives evidence that the above equations are valid for internuclear separations both large and small compared with ionic dimensions.

B. Binding Energy

The binding energy W as formulated by Rittner consists of interaction potentials (i.e., charge - charge, charge-dipole,

dipole-dipole, and an induced dipole potential energy), a repulsion term, a van der Waals term and kinetic energy terms. The kinetic energy terms represent differences in translational, rotational and vibrational energy between the molecule and free ions from which it is composed.

$$W = -\frac{e^2}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} - \frac{2e^2\alpha_1\alpha_2}{r^7} + Ae - r/\rho - \frac{c}{r^2} + \frac{h\nu_0}{2} + \frac{h\nu_0}{e^{h\nu_0/kt}-1} - \frac{kt}{2}$$

A is a constant, ρ is a repulsion constant, k is the Boltzmann constant, ν_0 is the vibration frequency, t is the temperature and c is the van der Waals constant.

By application of the condition that $\frac{dW}{dr} = 0$ and $\frac{d^2W}{dr^2} =$ k(force constant), W yields an expression for ρ as a function of e, r, $\alpha_1\alpha_2$, and c.

C. Data Employed

W and μ net on a theoretical basis come from the following sources:

1. r from electron diffraction studies[3]
2. k from spectral studies[4] hence ν_0 is determined.
3. α from crystal refractivities[5]
4. c is computed by the method of London[6] from ionization potentials[7] and electron affinity values[8].

D. Results of the Rittner Model

1. Repulsion Constants

The energy of repulsion in the gas is about 5 times that in the crystal.

2. Internuclear Distances

The calculated internuclear distances agree very well with the observed values and also show analogous regularities.

3. Binding Energy

Calculations of binding energies agree to within ± 3% of the experimental values (Cf. table).

4. Dipole Moment

Calculations agree well with experiments (Cf. table). Dipole moments generally increase with distance and are appreciably smaller than er values due to mutual polarization of the ions.

5. Vibrational Frequencies

Comparison with experimental data available (Vide infra for comments on reliability) was satisfactory (Cf table).

II. Recent Accurate Data and the Rittner Model

Rotational spectra provide very accurate values for internuclear distances and vibration-rotation interaction constants[9]. These constants describe the shape of the potential energy curve for the diatomic molecule. However, it is also necessary to have accurate values of the vibration frequency (Cf. equation for W). The Rittner calculations are compared with vibrational frequencies obtained from electronic spectra which are unreliable. Klemperer and Rice[10,11] obtain more accurate vibration values from high temperature IR spectra and comparison of his data with the ionic model proves fairly satisfactory.

However, increased deviation from the ionic potential energy curve will occur as r increases since the dissociated state consists of neutral atoms rather than of ions (vide infra). It also turns out that α values must be used which agree with dipole moments since experimental values make μ net appreciably less than observed. Therefore in principle it is not possible to calculate all the spectral constants from the Rittner model.

III. Evidence for Polymeric Species in the Vapor

Miller and Kusch[12] determined ratios of polymeric to monomeric species in the vapor phase (Cf. table) by analyzing velocity distributions in a molecular beam. This method is a definite improvement over previous work with molecular beam magnetic resonance spectra[13] and mass spectra[14].

Klemperer[10,11] however, finds no evidence for appreciable concentrations of dimer in the vibrational spectra even though the dimer has two IR active stretches.

It must be remembered, however, that the intensity of these stretches may be quite small and unobservable. Also, the molecular beam work was done at non-equilibrium conditions (i.e., solid → vapor) whereas that of Klemperer was done essentially at equilibrium (i.e., only vapor). It may be that the dimer is not stable for very long in the vapor state.

IV. Electronic Transitions in the Vapor

Berry and Klemperer[15] show that for large nuclear separations, the energy level corresponding to ions lies above the energy level corresponding to neutral atoms. Consequently the Rittner model is only valid for the strongly bound region where the ions are at small internuclear distances. The high temperature UV spectra obtained from the alkali halides indicates that this is indeed the case.

Berry[16] goes on to show mathematically that in the high temperature UV spectra of alkali halides, the reason for observation of definite bands in one case and a continuum in another. Physically, the reason stems from the fact that in the band spectrum, the electronic motions can follow the nuclear motion whereas in the continuum spectrum the electronic motions cannot follow the nuclear motions.

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TABLE OF DATA

	ω_e calc	ω_e elect spec	ω_e vib spec	dimer / mono	trim / mono	-W calc e v	-W exp e v	μ exp D	μ calc D	ea D	f
LiF	773								5.04	7.35	
Cl	705		662	3.6	.26				4.76	9.46	
Br	650		576	3.5	.29				5.11	10.28	
I	616	450	501						5.15	11.38	
NaF	477			.1	.05				7.99	9.60	
Cl	373	380	366	.36		5.44	5.56		8.71	11.91	
Br	321	315	302			5.26	5.34		8.84	12.53	
I	291	286	258	.38		4.91	5.03		9.33	13.78	
KF	410	390				5.94	4.98	8.62	8.06	10.42	.82
Cl	296	280	281	.12		4.94	4.98	9.53	10.09c	13.35c	.72
Br	241	231	213			4.76	4.76	10.85	10.46c	14.07c	.77
I	213	212	173e	.06		4.43	4.45	11.05	11.26c	15.42c	.72
RbF	361	340							8.33	11.09	
Cl	250	253	228			4.82	4.84		10.07	13.73	
Br	188		166e			4.62	4.61		10.56	14.50	
I	163		128e			4.42	4.30		10.75	15.46	
CsF	345	270				5.54	5.44	7.61	8.06	11.67	.65
Cl	229		209	.09		4.63	4.62	9.97	10.39	14.50	.65
Br	171	194	139e			4.50	4.43		10.49	14.89	
I	141	142	101e			4.28	4.28	12.1	11.29c	16.28c	.74

e=extrapolated c=calculated from α values at 900° to permit direct comparison of μ with experimental values.

RECENT ADVANCE IN THE CHEMISTRY AND STRUCTURE OF METAL CARBONYLS

John A. McLean April 15, 1958

I. INTRODUCTION

Metallic carbonyls have long been of interest to chemists inasmuch as they exhibit unique types of chemical bonding. The coordination number is not such as to satisfy a stable geometrical configuration, as in numerous octahedral complexes. Instead, the most important factor governing the coordination number seems to be the attainment of a closed shell of electrons. The simple mononuclear carbonyls and their derivatives are in general agreement with theories of hybridization. Spectroscopic and diffraction data have confirmed structures postulated on this basis (1, 2, 3, 4). The only polynuclear carbonyl which had been studied by diffraction technique before 1955 was $Fe_2(CO)_9$ (5). This lack of data has led to considerable confusion regarding the structures of these compounds.

II. NATURE OF BONDING

A. Carbon-Oxygen Bonds

The vibrational spectrum of nickel tetracarbonyl was studied by Crawford and Cross (6) who reported a value of 15.89×10^5 dynes cm^{-1} for the carbonyl bond stretching force constant. They concluded that since this value lies between the value associated with the double bond in formaldehyde (12.1×10^5) and the triple bond in carbon monoxide (18.6×10^5) the nickel tetracarbonyl C-O bonds have triple bond character. Nyholm (7) pointed out that a comparison of the force constant and bond length in $Ni(CO)_4$ with the values in formaldehyde is not justified since the hybridization of the carbon atom differs in the two cases. In formaldehyde the hybridization is sp^2, whereas in $Ni(CO)_4$ it is an sp hybrid. If the stretching force constants and bond lengths are compared with ketene or carbon dioxide where the hybridization is the same the agreement is very good. From this evidence double bonds seem to provide the best description of C-O bonds in carbonyls.

B. Metal-Carbon Bonds

The nature of the metal-carbon bond has been open to some question due to conflicting evidence of bond studies (8, 9, 10). Table I shows three typical carbonyls with relative bond strengths according to Pauling's scale.

TABLE I
Single Bond Strengths

Compound	Hybridization	Relative bond strength
$Cr(CO)_6$	d^2sp^3	2.92
$Fe(CO)_5$	dsp^3	2.72
$Ni(CO)_4$	sp^3	2.0

Infrared measurements (8) of nickel and iron carbonyls indicate that the Fe-C bond is stronger than the Ni-C bond. Thermochemical studies of Cable and Sheline(9) indicate that the Ni-C bond is stronger. Raman studies of King and Lippincott (10) are in agreement with the thermochemical studies. The two latter studies indicate the order one would expect if the metal-carbon bonds have double bond character. Chatt and Willimas (11) show that this partial double bond character can be achieved by utilization of the filled d orbitals of the metal and a vacant p orbital of the bivalent carbon atom.

III. STRUCTURAL DETERMINATIONS

A. Polynuclear Carbonyls

Structurally polynuclear carbonyls may be considered to be built up from polyhedra of mononuclear complexes. The structure is somewhat complicated by three alternative possibilities of joining these polyhedra: 1) the junction of two octahedra at the apex leads to a structure of metal-metal bonds, 2) junction at the edge represents a structure with two bridging carbonyls and 3) junction at the face represents a structure with three bridging carbonyl groups. Infrared spectroscopy is an invaluable tool for distinguishing between bridged and non-bridged structures since bridging carbonyls absorb at a lower frequency (7).

1. $Fe_2(CO)_9$: The structure of iron enneacarbonyl has been studied by X-rays (1), electron - diffraction (2) and infrared spectroscopy (8). All these investigations agree that the structure can be depicted by two octahedra joined face to face with three bridging carbonyls and three terminal carbonyls on each metal atom.

2. $[Fe(CO)_4]_3$: X-ray work by Brill (12) suggests two possible structures for iron dodecacarbonyl. The first has three octahedra joined at their faces and the second has three octahedra joined at their edges. Infrared studies by Sheline (13) favor the latter structure. Mills (14) found that the molecule is centrosymmetric in the solid state; his X-ray data support the former structure. Rundle (15) claims that both these structures are incorrect. His work indicates that the molecule consists of a trigonal arrangement of iron atoms, orientated randomly among positions 60° apart to produce an average center of symmetry.

3. $[Co(CO)_4]_2$: Unfortunately no X-ray data have been reported for the polynuclear cobalt carbonyls. On the other hand there seems to be general agreement in the interpretation of the infrared and ultraviolet spectra of dicobalt octacarbonyl (16, 17). The best structure assigned on the basis of group theory is a combination of two trigonal bipyramids joined at an edge.

4. $[Co(CO)_3]_4$: The structure for tetracobalt dodecarbonyl has not been determined. Original molecular weight determinations (18) indicated a tetramer. The chemical behavior indicates a salt-like structure such as $Co[Co(CO)_4]_3$. The infrared spectrum is in conflict with both these structures (17).

5. $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$: Infrared studies of these two decacarbonyls reveal no absorption band characteristic of bridge carbonyls (19, 20). Dahl (21) has shown by X-ray data that these structures consist of two octahedra joined at their apices.

B. Carbonyl Hydrides

The known metal carbonyl hydrides are $HRe(CO)_5$, $H_2Fe(CO)_4$, $H_2Os(CO)_4$, $HRh(CO)_4$ and $HIr(CO)_4$. Of these, only the iron and cobalt compounds have been studied in detail. Electron diffraction studies by Ewens and Lister (22) indicate that the four CO groups are arranged tetrahedrally about the metal atoms. The position of hydrogen has been open to some question. Infrared studies (23, 24) indicate a metal hydrogen mode at 703 cm^{-1} but no C-H or O-H stretch. NMR studies substantiate the infrared findings. A chemical shift of 15.5 ppm relative to water indicates a much greater electron density about the hydrogen nucleus than is found when hydrogen is bound to oxygen or carbon atoms. A Molecular Orbital treatment (25) has been used to support an attractive bridge model of cobalt carbonyl hydride which bonds the hydrogen atom with seven other atoms. Recently Liehr (26) has used symmetry arguments to propose structures for iron and cobalt carbonyl hydrides. The proposed structures predict the possibility of a hindered rotation of the bonded hydrogen atoms. The hydrogen is bonded to the d_{z^2} or the $d_{x^2-y^2}$ orbital of the metal atom in the case of cobalt and to both these orbitals in the case of iron.

X-ray studies (27) of metal cyclopentadienyl carbonyl compounds have shown a rather unusual type of metal-metal linkage. Bis-cyclopentadienyl metal hexacarbonyls of Mo and W are crystallographically isomorphous. The shortest metal-metal distance has been found to be 3.24 Å in W and 3.28 Å in Mo. These distances indicate that the molecules are not present as dissociated monomers. This result is in accord with the observed diamagnetism of these compounds and their molecular weights in solution (28).

IV. REACTIONS OF CARBONYLS

A. Metallo-Organic Complexes

It has been found that the two bridge carbonyls in dicobalt octa-carbonyl can be replaced by acetylenes (29, 30). If the alkyne contains two triple bonds, each triple bond reacts with a mole of dicobalt octacarbonyl (29). It is not possible on the basis of infrared spectra, magnetic susceptibility, or dipole moment measurements to predict the correct structures of these compounds.

The anion of iron hydrocarbonyl reacts with acetylenes to give a bridged iron complex whose structure differs considerably from the cobalt complex (31). In the cobalt complex each acetylene contributes four of its pi electrons to the pi bonding of the complex. Clarkson (31) suggests that the structure of the iron compound bears a close relationship to iron enneacarbonyl.

Sternberg (32) has shown that the complex formed by iron pentacarbonyl and dimethylacetylene decomposes in acid solution to give durohydroquinone. On the basis of this experimental evidence a new structure is proposed for the iron carbonyl hydride-acetylene complex. This structure contains a cyclobutadiene ring held to the metal by pi bonds.

B. Reactions In Certain Amines

Dicobalt octacarbonyl reacts with a variety of Lewis bases according to the general equation (33, 34):

$$3[Co(CO)_4]_2 + 12B \rightarrow 2[Co(B)_6][Co(CO)_4] + 8CO$$

Sternberg (35) studied the mechanism of the reaction of iron pentacarbonyl with different amines. Conductance measurements show that the carbonyl dissociates in to charged species:

$$2Fe(CO)_5 \rightleftharpoons [Fe(CO)_6]^{++} + [Fe(CO)_4]^{=}$$

The ability of an amine to cause ionization of iron pentacarbonyl is dependent on two main factors: (a) The availability of the lone pair of electrons on nitrogen for bonding or charge neutralization, a polar effect; and (b) the presence of many or bulky substituents on nitrogen which prevents the pair of electrons from reaching the site of reaction, a steric effect. Hieber (36) has recently reported that the stoichiometry of the iron complex formed between iron dodecacarbonyl and ethylenediamine depends on the temperature.

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ISOTOPIC TRACERS IN INORGANIC CHEMISTRY

J. A. Chandler April 22, 1958

I. Introduction

The use of isotopic tracers has increased greatly in the last two decades as more synthetic radioisotopes have been produced, and as stable isotopes of the lighter elements have been made available. Equally important to this increased usage has been the development of highly precise instruments for the assaying of both radioactive and stable isotopes. Isotopic tracers are now available to chemists for the study of reaction mechanisms, structures, bond lability, and many other topics. Since the uses of isotopic tracers in inorganic chemistry cover a broad area, only a few specific examples may be covered. For those who wish more information, reference 1 is recommended.

II. Applications

A. Structures

1. One of the earliest uses of a synthetic radioisotope was the determination of the non-equivalence of the sulfur atoms in thiosulfate (2). This was proven through the following series of reactions:

$$Na_2SO_3 + S^* \rightarrow Na_2S^*SO_3$$

$$Na_2S^*SO_3 + 2HCl \rightarrow S^* + SO_2 + 2NaCl + H_2O$$

$$Na_2S^*SO_3 + 2AgNO_3 \rightarrow Ag_2S^*SO_3 + 2NaNO_3$$

$$Ag_2S^*SO_3 + H_2O \xrightarrow{\Delta} Ag_2S^* + H_2SO_4$$

2. The proof of the non-equivalence of the sulfur atoms in the S_2O_3 molecule was similarly shown (3):

$$S^* + SO_3 \rightarrow S^*SO_3 \xrightarrow{C_4H_8O_2} S^* + C_4H_8O_2 \cdot SO_3$$

3. During a study of the Ni^{*+2}-$Ni(CN)_4^{-2}$ system, it was found that the nickel cyanide which precipitates from this mixture contains non-equivalent nickel atoms (4). If the nickel cyanide is treated with dimethylglyoxime, one-half of the nickel is recovered as $Ni(DMG)_2$. The $Ni(DMG)_2$ contains all of the activity. This was interpreted by formulating nickel cyanide as $NiNi(CN)_4$.

4. When Pb_3O_4 is made from Pb^{*+2} and Pb^{+4} and is subsequently decomposed by cold KOH, essentially no exchange occurs (5, 6). However, when hot KOH, HNO_3, or $NH_4C_2H_3O_2$ is used, 30 to 100% exchange occurs. These results emphasize the need for a careful choice of separating agents even when non-equivalence of atoms is present.

5. Using radiotracer techniques, the sulfur atoms of S_4N_4 have been shown to be equivalent (7). This is in agreement with both the proposed cage (8) and cradle-like structures (9). The equivalence of the sulfur atoms was shown by preparing S_4N_4 from a S (II) and a S* (IV) compound and then decomposing the sulfur nitride to other S (II) and S (IV) compounds. The activity was equally distributed. S_4N_4 was prepared by the reactions $(ClS^*N)_3 + (SNH)_4$ and $(ClS^*N)_3 + S_7NH$. The S_4N_4 was decomposed in the following ways:

$$S^*_4N_4 + PbI_2 \xrightarrow{NH_3(l)} Pb(NS^*)_2$$

$$S^*_4N_4 + HgI_2 \xrightarrow{NH_3(l)} HgN_2S^*$$

$$S^*_4N_4 + 4C_5H_{10}NH \rightarrow 2(C_5H_{10}N)_2S^* + 2S^*(NH)_2$$

B. Detection of Bond Cleavage and Reaction Mechanisms

1. During a study of the reaction $Co(NH_3)_5Cl^{+2} + Cr^{+2} \rightarrow CrCl^{+2} + Co(NH_3)_5^{+2}$, it was found that if the reaction is carried out in the presence of Cl^{*-}, less than 1% of Cl^{*-} appeared in $CrCl^{+2}$ (10, 11). As both $CrCl^{+2}$ and $Co(NH_3)_5Cl^{+2}$ exchange very slowly with Cl^{*-} in solution, it was reasoned that the Co-Cl bond must break at the same time the Cr-Cl bond is formed and that the electron transfer reaction must procede through the acitivated complex $[(NH_3)_5Co\text{-}Cl\text{-}Cr]^{+4}$.

2. The reactions $Co(NH_3)_5(OH_2)^{+3} + NO_2^- \rightarrow Co(NH_3)_5ONO^{+2} + H_2O$ and $Co(NH_3)_5ONO^{+2} \rightarrow Co(NH_3)_5NO_2^{+2}$ have been studied using isotopic tracers (14). It had been postulated that the mechanism of the reactions is the following (13):

a) $2HNO_2 \rightarrow ONONO + H_2O$

b) $R_5CoOH_2^{+3} + ONONO \rightarrow R_5CoONO^{+2} + HNO_2 + H^+$ (no co-O bond breakage)

c) $R_5CoONO^{+2} \rightarrow R_5CoNO_2^{+2}$ (intramolecular)

Using O^{18} enriched water, it was shown that reaction (b) procedes as postulated. Non-exchange of $(NH_3)_5CoONO$ and $(NH_3)_5CoNO_2$ with NO_2^- in solution indicates that reaction (c) is also correct. This is also supported by the solid state conversion of the nitrito to the nitro complex (12).

3. The reaction $HN_3 + HNO_2 \rightarrow N_2O + N_2 + H_2O$ has been thoroughly investigated (15-17). The reaction was shown to procede as $\overset{aba}{HNNN} + \overset{c}{HNO_2} \rightarrow \overset{ac}{NNO} + \overset{ab}{NN} + H_2O$. This was done by carrying out the reaction a) with $HN^{15}O_2$, b) with $HN^{15}NN^{15}$, and c) by analyzing the nitrous oxide formed utilizing the isotopic reaction:

$$NN^{15}O + NaNH_2 \xrightarrow{20\%} NaNN^{15}N \xrightarrow{HI} NH_3 + NN^{15}$$

$$\xrightarrow{80\%} NaNNN \xrightarrow{HI} NH_3 + N_2 + N^{15}H_3 + NN^{15}$$

4. The reaction of hydroxylamine and nitrous acid to give nitrous oxide and water has been studied with the purpose of determining the reaction mechanism and the nature of intermediate species (18). The reaction was carried out with $NH_2OH\cdot HCl$ and $NaN^{15}O_2$ in O^{18} enriched water. At the natural pH of the reaction, equal amounts of $NN^{15}O$ and $N^{15}NO$ are formed. At pH 1 however, the $NN^{15}O/N^{15}NO$ ratio is 2. This is consistent with the following mechanisms:

$$NH_2OH + HN^{15}O_2 \rightarrow HON{=}N^{15}OH \rightarrow N^{15}NO + NN^{15}O$$

$$NH_2OH + HN^{15}O_2 \rightarrow H(HO)NN^{15}O \rightarrow NN^{15}O$$

The second path becomes more important as the pH is lowered.

C. Solvents

One of the basic postulates of the solvent system concept is that solvents capable of forming conducting solutions undergo self-ionization. While this is an attractive explanation, it is frequently difficult to verify experimentally. Consider the case of phosgene, whose self-ionization may be represented as $COCl_2 = CoCl^+ + Cl^-$. If this truly represents the solvent phosgene, tagged chlorine ions added to the solvent should be rapidly incorporated into the phosgene. This system has been investigated using $AlCl_3$*, NaCl*, $CaCl_2$*, NaCl + $AlCl_3$*, and $CaCl_2$ + $AlCl_3$* (19). In all cases the exchange is very slow, and there is essentially no exchange with NaCl* and $CaCl_2$*. This data is interpreted in terms of little or no ionization of phosgene. The $AlCl_3 \cdot COCl_2$ compound is evidently molecular in nature as the Cl^{*-} exchange is no more rapid than that of the solution of $AlCl_3$* in phosgene.

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MOLECULAR SIEVES

Harlan D. Frame, Jr. April 29, 1958

I INTRODUCTION

The use of instruments or techniques to carry out specific separations has always intrigued chemists. Few methods offer more selectivity than molecular sieves. The definition of a molecular sieve requires that it preferentially retain one of several species upon contact with a mixture and that it release this species upon completion of the experimental cycle.

To achieve this objective it is necessary that some diffusion medium be found in which partially or wholely different diffusion velocities are attained. A substance or series of substances which has definite and constant-sized pores or channels should fulfill this requirement. The 35 minerals known as zeolites contain apparently physically-trapped water in regular channels, which when removed leaves as much as 56% pore volume available for occlusion of species with critical molecular dimensions less than the diameter of the pore (assumed circular). Only a robust three-dimensional lattice will hold its open structure under such rigorous treatment, and only a physically strong structure will serve as an efficient molecular sieve. The critical molecular dimension may be defined as "the diameter of the smallest cylinder which will accomodate a model of the molecule constructed using the best available van der Waals radii bond angles and bond lengths (1)."

II PREPARATION

Natural zeolites may be heated (up to 400°C.) in vacuum for the removal of the water leaving the activated sieve (2). Synthetic crystallin sieves may be prepared by one of two general methods. The first involves the autoclave heating of a natural mineral with an excess (to assure uniformity) of a mineralizing agent (e.g., analcite plus barium chloride at 400°C.) followed by removal of the interstitially incorporated salt by high temperature extraction with distilled water. Vacuum removal of the water again leaves the activated sieve. An alternate procedure makes use of a synthetic gel in place of the natural mineral (3,4).

III PROPERTIES

The essential properties of some of the more important zeolitic sieves used to date are listed in Table I (5,6,7,8).

Two factors determine the completeness of a separation: the ease of occlusion of a given species, and its relative affinity for the sieve when once occluded. The former is controlled by the (stearic) critical diameter of the species, and its (presumably thermal) mobility. Thus, since chabazite cannot occlude isobutane

Class	Sieve	Ideal Formula	Water content*	Critical diameter	Sorption Characteristics
A	Faujasite	$(Na_2,Ca)Al_2Si_5O_{14}\cdot 10H_2O$	56%	6Å	isoparafins, e.g., neopentane and higher
B	Chabazite,	$(Ca,Na_2)Al_2Si_4O_{12}\cdot 6H_2O$	50		no sorption of iso-parafins or aromatics, n-parafins slowly (C_3 to C_7) C_1 and C_2 and molecules of smaller crit. dia. rapidly
	Gmelinite,	$(Na_2,Ca)Al_2Si_4O_{12}\cdot 6H_2O$	50	4.9	
	synthetic	$BaAl_2Si_4O_{12}\cdot nH_2O$			
C	sodium-rich Mordenite	$(Ca,K_2Na_2)Al_2Si_{10}O_{24}\cdot 6\cdot - 6H_2O$	33	4	no sorption of iso-n-parafins, or aromatics; sorbs CH_4 and C_2H_6 slowly; sorbs N_2, O_2 and smaller crit. dia. molecules rapidly
D	potassium-rich Mordenite, Levynite	$CaAl_2Si_3O_{10}\cdot 5H_2O$	40	3.8	CH_4 and C_2H_6 slowly or in negligible amounts; N_2 and molecules of smaller crit. dia. sorbed
Linde synthetics "Type A"		$(Na_2,Ca)_6[(AlO_2)_{12}(SiO_2)_{12}]\cdot - 27H_2O$			
	sodium form		45	4	
	1/3 calcium		48	5	
"Type X"		$(Na_2,Ca)43[(AlO_2)_{86}(SiO_2)_{106}]\cdot - 267H_2O$		10-13	

* cm^3 of liquid H_2O displaced from 100 cm^3 of crystals for first four classes and g H_2O absorbed per 100 g activated zeolite in last two clases

in the series:

$$CHCl_3,\ CH(CH_3)_3,\ CHBr_3,$$

it fails to occlude chloroform and bromoform (5). In the n-paraffin series, since chabasite occludes propane it also occludes large amounts in the series up to n-heptane, but the occlusion rate decreases as molecular weight increases (9,10).

The second of these factors is demonstrated in the argon-krypton separation by mordenite where the sieve is so contaminated by krypton that no separation is possible (11). Similarly, acetone contaminates chabazite for n-heptane.

Several techniques are available for altering the occlusion characteristics of a sieve.

Since removal of the water molecules created the channel in the first place, failure to remove some of the water or replacing some of it will cut down the size of the channel (12).

In the diffusion equation:

$$D = D_0\ e^{-E/RT},$$

where: D = diffusion coefficient
E = activation energy,

a D_0 and an E value may be assigned, and it then becomes apparent that lowering the temperature will spread the D values for two species, all other factors being equal (13).

Cation interchange may also be used to alter lattice dimensions. This is usually achieved by modification of the usual preperative procedure. An excess of the replacing salt is used during the autoclaving cycle. Alternately, a vapor phase reaction (e.g., ammonium chloride) may be used. A special case of ion exchange alteration is the formation of a large-channeled sieve by ammonium exchange followed by oxidation to the hydrogen form with occluded oxygen (14).

IV EXPERIMENTAL TECHNIQUES

Two general methods are available to effect a given separation: static and continuous flow. When total separations are possible (e.g., dehydration of a molecular species whose critical diameter is greater than 6 Å) either method will suffice. Partial separations call for stepwise fractionation or a continuous, chromatographic technique (15,16).

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THESIS ABSTRACT

KINETICS, STEREOCHEMISTRY, AND MECHANISM OF THE CHLORIDE ION EXCHANGE WITH CIS-DICHLORO-BIS-ETHYLENEDIAMINE-PLATINUM(IV) ION.

Gordon L. Johnson May 13, 1958

The exchange of chloride ion with cis-dichloro-bis-ethylenediamine-platinum(IV) ion was studied and found to be first order in concentration of chloride ion, of cis-dichloro-bis-ethylenediamine-platinum(IV) ion, and of the catalyst, bis-ethylenediamine-platinum(II) ion. The experimentally measured heat of activation and the entropy of activation are 8.01 kcal. $mole^{-1}$ and -23.76 cal. $deg.^{-1}$ $mole^{-1}$, respectively. The specific rate constant at 30°C is 6.014×10^{1} $liter^{2}$ $mole^{-2}$ $sec.^{-1}$

The exchange rate is not appreciable at low concentrations of chloride ion except in the presence of a catalyst such as the bis-ethylenediamine-platinum(II) ion or the tetrammine-platinum(II) ion.

From infrared and X-ray studies, there is no indication of cis to trans conversion; and from optical rotation measurements on the l-cis-dichloro-bis-ethylenediamine-platinum(IV) ion, there is no loss of optical activity under the conditions of the exchange study. Also, aquation of cis-dichloro-bis-ethylenediamine-platinum(IV ion is negligible under these conditions. Therefore, the exchange appears to take place with retention of configuration and without the complication of aquation.

The exchange reaction is pictured as taking place between the chloride ion and an activated binuclear complex by means of a simple bimolecular transfer of chloride ions. The binuclear complex consists of the cis-dichloro-bis-ethylenediamine-platinum(IV) ion attached to the planar catalyst molecule by a chlorine atom from the platinum(IV) system.

THESIS ABSTRACT

THE SYNTHESIS AND PHYSICAL CHARACTERIZATION OF SEVERAL METAL CONTAINING POLYMERS

Malcolm L. Judd May 13, 1958

The advances of modern technology have created an urgent need for versatile construction materials. Specifically, a critical need has developed in the aircraft industry for materials which are tractable up to the temperature of 900° F. The known organic polymers do not meet the desired specifications.

The present study has been concerned with the synthesis and physical characterization of several metal containing polymers in which the metal ion is held in the polymer through coordinate bonds.

Chelate polymers containing bis-amino acids, tetrafunctional derivatives of benzidine, bis- α -amino phenols as well as bis-8-hydroxyquinolines have been investigated:

a) bis-amino acids

α, α'-diaminosebacic acid

N, N' diacetic acid - N, N' bis-(hydroxyethyl) ethylenediamine

b) tetrafunctional derivatives of benzidine

α, α' benzidine disulfonic acid

N, N' benzidine diacetic acid

c) bis α-aminophenols

2, 2-bis-(3-hydroxy-4-amino-phenyl) propane

bis-(3-hydroxy-4-amino-phenyl) sulfone

bis-(3-hydroxy-4-amino-phenyl)

d) bis-8-hydroxyquinolines

bis-(8-hydroxy-5-quinolyl) methane

bis-(8-hydroxy-5-quinolyl)

2,2-bis-(8-hydroxy-5-quinolyl) propane

bis-(8-hydroxy-5-quinolyl) sulfone

bis-(8-hydroxy-5-quinolyl) sulfide

The most promising results have been obtained with the polymeric bis-8-hydroxyquinolines.

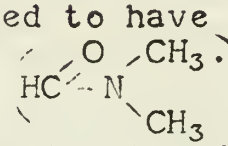
The thermal and hydrolytic stabilities of some metal chelates of β-aminoglutaric acid as well as the thermal stabilities of some metal chelates of imino diacetic acid were determined.

A thermal gravimetric balance, easily constructed from ordinary laboratory equipment, is described.

Thesis Abstract

A Spectroscopic Study of the Basicity of Amides in Iodine-Amide Systems

C. D. Schmulbach May 20, 1958

Iodine and the other halogens are reported to have an unusually high solubility in dimethyl formamide  . This work was undertaken to provide insight into the nature of interaction between basic amide solvents and iodine. Examination of the ultraviolet and visible spectra of carbon tetrachloride solutions of amides and iodine revealed the presence of weak, easily dissociated, 1:1 molecular charge-transfer complexes. An isosbestic point is observed when the iodine concentration is kept constant and the dimethyl acetamide (DMA):I_2 mole ratio is maintained between 1000:1 and 10:1. When this ratio is increased to 10,000:1, new absorption bands which are attributed to the triiodide ion are observed at 367m and 297m. The time-dependent increase in optical density of the triiodide peak parallels earlier reported changes in the conductance of the pyridine-I_2 system. The triiodide peak is present in the dimethyl formamide (DMF)-I_2 system with the DMF:I_2 mole ratio as low as 80:1.

The amide carbonyl stretching frequency is sensitive to electronic environment making the amide-I_2 systems particularly amenable to an infrared study. The frequency of the uncomplexed carbonyl stretching mode is shifted to lower frequencies upon the addition of an excess of iodine. This indicates that bonding to iodine is through the carbonyl oxygen instead of the nitrogen. There is a linear relationship between Taft's σ^* values and this shift in frequency in the $R-\overset{O}{\overset{\|}{C}}-N(CH_3)_2$ series where (R-) is H-, CH_3-, C_2H_5-, but the shift is greater than expected when the R- group is phenyl. The equilibrium constants of this series give no correlation. The heats of reaction are expected to vary in the same manner as the frequency shifts. The random variation in the equilibrium constants is believed to be due to an entropy effect. Triiodide ion is shown to be absent in the solutions studied by infrared spectroscopy.

The equilibrium constants, at various temperatures, of the dimethyl acetamide-iodine complex are found to be smaller when determined by ultraviolet-visible spectroscopy than when measured by infrared spectroscopy. At the same time, the heats of reaction and entropies of reaction are larger negative values when calculated from ultraviolet-visible data. A large and varied excess of amide is added to a carbon tetrachloride solution of constant iodine concentration in the U.V. experiments. Under such conditions, there is a large variation in the nature of the solvent. The increase in dielectric of the solvent would tend to encourage the formation of ion pairs and ionic species. In addition, the assumption that the Beer-Lambert law is valid for the iodine band in all concentrations of amide is questionable, for it is known that the extinctiob coefficient is a function of the dielectric constant of the medium.

The infrared measurements require a large excess of non-polar iodine in carbon tetrachloride solutions of the amide, thus avoiding drastic changes in the dielectric of the system.

STEREOCHEMICAL STUDY OF SOME COMPLEX IONS

Laurence F. Dempsey

May 20, 1958

Many platinum(II) tetracovalent complexes are known. Because the platinum(II) ion possesses eight electrons in the 5d orbitals, the Pauling theory of hybrid orbitals would predict that either sp^3 (tetrahedral) or dsp^2 (planar) complexes could be found. Although cis-trans isomerism, the trans-effect, optical isomerism, x-ray determinations, magnetic moments, dipole moments, etc. indicate the existence of many planar complexes of platinum(II) in which the hybridization is presumably dsp^2, no definite evidence for the existence of a tetrahedral platinum(II) complex has been found.

Mann and Pope prepared a platinum(II) complex with β,β',β"-triaminotriethylamine, $(:NH_2CH_2CH_2)_3N:$, in which the ratio of metal to base is 1:1, and they concluded that because of the geometry of the base, the platinum(II) complex could not be planar. No evidence beyond the chemical analysis of the compound was given to indicate that the platinum(II) ion is tetrahedral.

An attempt is in progress to prepare a pure sample of $[Pt(NH_2CH_2CH_2)_3N]Cl_2$ in order to determine the number of ions present by means of equivalent conductance measurements, and in order to determine the molecular weight of the complex. First attempts to make this compound according to the directions of Mann and Pope produced only platinum black; it was found, however, that if the amine hydrochloride is added to a solution of potassium chloroplatinate(II), the platinum complex can be made by the very slow addition of a solution of potassium hydroxide. If the solution is evaporated to dryness, a film which does not redissolve in water is formed. If a soluble iodide is added to the solution, $[Pt(NH_2CH_2CH_2)_3N]I_2 \cdot 2H_2O$ precipitates, and when dried, the iodide does not redissolve in water. An x-ray powder pattern of this compound showed that these samples are completely amorphous. At the moment it is anticipated that the platinum complex will prove to be dimeric or polymeric in which the platinum is planar.

It is well known that rotation about the central bond in certain derivatives of biphenyl containing large functional groups in the 2,2'-positions is restricted by the mechanical interference of these large substituents. In this work, 2,2'-diaminobiphenyl, abbreviated dabp, is to be coordinated to a metal atom which will act as a substituent to prevent free rotation in the biphenyl molecule with the result that the two phenyl rings will not be coplanar, and that the molecule will be optically active.

Middleton was able to prepare complexes of the type: $[M(dabp)_2]Cl_2$, where M = Cu, Co, Ni, Zn, Hg, or Cd, by dissolving the anhydrous metal chloride and the free amine in absolute alcohol; the complex precipitates almost immediately. These complexes were not used in this study because of their instability in water, and because of the formation of more than two isomers. Middleton also was able to prepare $[Coen_2dabp]Cl_3$ which was later resolved by McCullough. Because of the three chelate rings in this compound, however, the cobalt is asymmetric, and contributes to the optical activity. $[Co\{(NH_2CH_2CH_2)_3N\}\{dabp\}]Cl_3$ is being prepared in order to produce a complex in which the cobalt is symmetric, and the total optical activity of the complex will be due to the restricted rotation in the coordinated biphenyl molecule.